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PRINCIPLES OF HIGH-POLYMER THEORY AND PRACTICE

Fibers · Plastics · Rubbers · Coatings · Adhesives

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Principles of HIGH-POLYMER THEORY AND PRACTICE

FIBERS · PLASTICS · RUBBERS · COATINGS · ADHESIVES

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PRINCIPLES OF HIGH-POLYMER THEORY AND PRACTICE

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PREFACE

This is a textbook on the principles of high-polymer theory and practice and hence covers materials composed of molecules of high molecular weight, whether they be fibers, plastics, rubbers, surface coatings, or adhesives. Its purpose is to present a broad, coordinated treatment of a field in which about one-third of all American chemical engineers and chemists are currently employed. This can be done only by demonstrating how fundamentals of physics, chemistry, and engineering may be applied universally to the materials in question.

In teaching the subject to college students, the authors found that none of the many excellent books in print were suitable as a text for the course envisioned because they were too highly specialized with respect to individual phases or facets of the subject. Many were limited to fibers, plastics, or rubbers as though these were fields entirely apart. Some proved to be descriptive and factual treatments of industrial processing and manufacture, at the technical-institute rather than the college level. Others emphasized chemistry but neglected the physico-chemical, rheological, and engineering aspects. Still others, mainly at the graduate level, were devoted so completely to physical chemistry or rheology that they were unsuited as texts although very valuable for supplementary reading.

The intention of the more comprehensive approach here employed is to give insight into underlying phenomena and to preserve the broad viewpoint throughout, so that what the reader learns about fibers he will immediately recognize to be translatable also into terms of plastics, rubbers, surface coatings, and other high-polymer products. Although no attempt was made to cover all the chemical high-polymer families, the examples chosen for the illustration of basic principles cover a wide range of materials, as is evident from the index.

Before taking this subject, which should normally not be taught before the junior or senior year, the undergraduate has usually had adequate training in inorganic and organic chemistry but not in physical chemistry or mechanics of materials. The subject demands wider knowledge of these latter than can ordinarily be included in beginner's courses, and the chemical engineer or chemist starting in the field of high polymers must realize from the very outset that unless he grounds himself thoroughly, he will work under a severe handicap. A purely "chemical" approach is

an inadequate basis for research and development in this field today. Consequently, sufficient space is devoted to physicochemical, rheological, and structural principles, not only to make up for the student's usual lack of information about them, but also to give them their true importance in relation to the subject as a whole.

During eight years of evaluation and experimentation on the teaching of this subject, the authors have found that it is of outstanding pedagogical value in the undergraduate as well as graduate curriculum. It enables the student to correlate many phases of his previous training and envision the extension of pure to applied science to an unusual degree.

The authors have attempted to suit the text to both undergraduate and graduate courses of varying length. Thus, Chaps. 1 to 3 were so written that Chaps. 5 and 6 may to a large extent be by-passed if restrictions are imposed by time or the student's prior training. Chapters 9 to 15 may also be regarded as optional in the face of time limitations, permitting emphasis on special subdivisions of the field. Cross references are used copiously throughout the text to facilitate such optional selections.

References to literature have been handled in a somewhat unusual manner. In college texts on old established subjects, references to treatises and monographs are sufficient to guide the student properly in his further reading. In a similar manner, a number of books in this field, varying from practical handbooks to graduate-level treatments of particular phases, are listed both at the ends of appropriate chapters and in Appendix A. But owing to the relatively recent development and crystallization of this subject, such references are in themselves insufficient. However, it was neither feasible nor appropriate to include full lists of original investigations as is the custom in monographs. Therefore, whenever necessary, the authors selected recent review articles and listed them at the ends of the chapters. In addition, whenever possible, figures and tables were selected from books and articles deemed particularly worthy of further reading. The authors feel that this plan successfully guides the student to fruitful and efficient reading.

We are deeply grateful to the many authors, investigators, companies, and publishers who have granted permission to use data and illustrations. We are especially indebted to Dr. W. O. Baker for devoting time to the express purpose of supplying new material. Our thanks also go to our colleague, Prof. S. Sonkin, for advice on part of the manuscript and to Donald Peaceman for reading it critically from the student's viewpoint.

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CHAPTER 1

INTRODUCTORY DEFINITIONS AND CONCEPTS

100. The subject of high polymers is the subject of large molecules. By large molecules are meant those with molecular weights of the order 10^5 to 10^6 . We are clothed, housed, and fed by high polymers. The body tissues are high polymers, and the very life processes are to a considerable extent high-polymer reactions. Many important materials, natural and synthetic, organic and inorganic, are high polymers. A few examples are listed in Table 1-1. All fibers and rubbers and most plastics, surface coatings, and adhesives are high polymers.

101. The Structure of High Polymers. Accumulated evidence shows that very large molecules do not possess an infinitely complex and ramified structure. Rather they prove to be large structures built up by the successive repetition of small, simple units, much as a chain is constructed of links or a wall of bricks. Thus, a cellulose molecule may have a molecular weight of 486,000. Upon investigation, its empirical formula proves to be $C_6H_{10}O_5$, a chemical unit whose molecular weight is 162. Further study reveals that this unit as it occurs in cellulose has a definite, invariant structure (Table 1-1) and that a cellulose molecule is a chain of such units. The structure of this chain may be variously represented as



or, more conveniently, $(C_6H_{10}O_5)_n$.

The chemical-structural unit of a polymeric molecule is called the *mer*. (Mer comes from the Greek and means *part*.) In this text, the term mer will mean always *the simplest chemical-structural unit in terms of which the polymer may be expressed*. Thus, the mer of cellulose is the $C_6H_{10}O_5$ unit shown in detail in Table 1-1. Since the mer has a definite structure and chemical composition, it has a molecular weight, which will be called the *mer weight*.

A *polymer*, as the word implies, is merely a molecule containing many mers. The *degree of polymerization* is the number of mers in the polymer. It is designated by the symbol n as in Table 1-1 or by the abbreviation D.P. By definition, the molecular weight is the product of the mer weight and the degree of polymerization. Conversely, the degree of polymerization is the molecular weight divided by the mer weight. For

TABLE 1-1. EXAMPLES OF HIGH-POLYMER MATERIALS

Material	Empirical formula	Structure of mer	Polymer type
Cellulose	$(C_6H_{10}O_5)_n$		Linear
Natural (Hevea) rubber	$(C_5H_8)_n$		Linear
Gutta-percha	$(C_5H_8)_n$		Linear
Silica (quartz)	$(SiO_2)_n$		Space
Diamond	$(C)_n$		Space
Polyvinylidene chloride	$(C_2H_2Cl_2)_n$		Linear
Polyethylene	$(CH_2)_n$		Linear
Methyl silicone	$(C_2H_6SiO)_n$		Linear
Polyhexamethylene adipamide (nylon)	$(C_{12}H_{22}N_2O_2)_n$		Linear
Polyethylene tetrasulfide (Thiokol A)	$(C_2H_4S_4)_n$		Linear (before vulcanization)

the previously cited cellulose molecule whose molecular weight is 486,000, the degree of polymerization is $486,000/162$, or $3,000$.

Representing the mer by M , a polymer has the composition $(M)_n$. If the mers are joined in line, $-M-M-M-M-$, etc., the molecule is a typical *linear*, or *chain*, *polymer*. If they are joined in a three-dimensional network as shown in Fig. 1-1c, it is a typical *space polymer*. As will be seen later, these two structural types have fundamentally different properties, and it is of the utmost importance to know to which type a given polymer belongs. A space polymer may be pictured as linear chains joined in space by chemical cross-links.

Some chain polymers are not strictly linear. They are branched as represented in Fig. 1-1b. Branching must not be confused with space

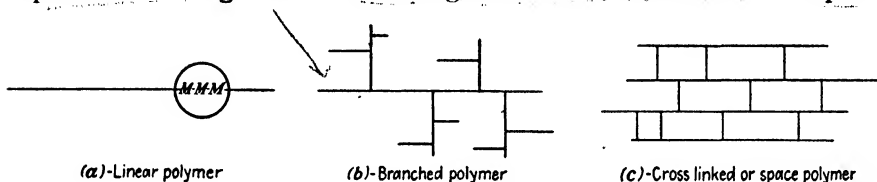


FIG. 1-1. Schematic representations of high-polymer structures.

polymerization. In branching, the molecules are essentially separate and discrete. In a space polymer, chains are cross-linked into networks of theoretically infinite size, forming supermolecules.

102. Seat of Special Properties of High Polymers. High-polymeric substances exhibit behaviors and properties that are different from those of ordinary low-molecular-weight compounds. The differences are a matter of degree rather than of kind. They are physical and mechanical rather than chemical. For example, high polymers are often plastic or highly viscous masses that can be spun into fibers or molded to shape in dies by the application of heat and pressure, thus affording very useful artifacts that cannot be produced from low-molecular-weight materials. As the subject unfolds, it will become increasingly evident that the unique properties of high polymers are attributable directly and solely to the unusual shape and large size of the molecules. Large size and surface result in a large total force of attraction between molecules, which in turn accounts for unusual physical and mechanical behaviors. Also, the length of a typical chain polymer is hundreds or even thousands of times greater than its other measurements. Such a molecule can undergo enormous changes in dimension in passing from a straightened to a coiled or folded condition. In ordinary small nonpolymeric molecules, this cannot happen.

103. Polymerization. Natural high polymers are formed in geological processes and the life processes of plants and animals by mechanisms that

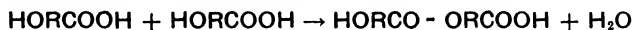
are most often a matter of conjecture. Polymers may also be synthesized. A synthetic high polymer is made by causing a great number of small molecules called *monomers* to join chemically into large molecules. The monomers may be all of one kind or of different kinds, and side products may or may not form.



In Eq. (1-1), all the monomers are identical, and the polymer is the only product formed. In Eq. (1-2), A and B are monomers of two different molecular species, which combine to form a polymer $(C)_n$, water being split out as a side product in the process.

For polymerization to occur, it is essential that the monomers possess the correct number and kinds of functional (active) groups. The chemical nature must be such that each monomer can "hook up" chemically with at least two others. If this condition is met, molecular growth can proceed indefinitely by a stepwise process. Accordingly, in this text, Carothers' definition of polymerization will be used, *viz.*, *polymerization* is an intermolecular combination functionally capable of proceeding indefinitely.

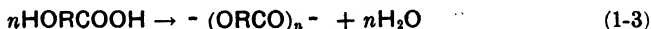
As an illustration, consider a hydroxycarboxylic acid whose structure is HORCOOH. It has two active, or functional, groups, both of which can participate in esterification. Under the proper conditions, two of these monomers can be made to react.



The resulting dimer is an ester roughly twice as large as the original monomer and at one end is still an alcohol and at the other a carboxylic acid. It can react with two more monomers to form a tetramer.



This stepwise process may be repeated many times. In theory, it can go on indefinitely. At any rate, a high-polymer ester forms; and if the end groups of the latter are ignored, the reaction can be represented as follows:

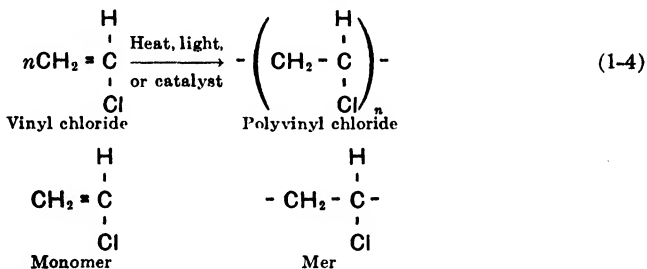


The reaction is thus a typical polymerization in accordance with Carothers' definition.

The structures and the modes of formation of a great many high polymers are now sufficiently well known to reveal that there are two fundamental polymerization mechanisms, addition and condensation.

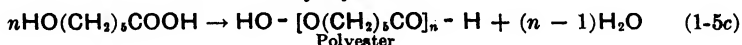
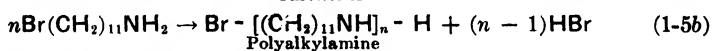
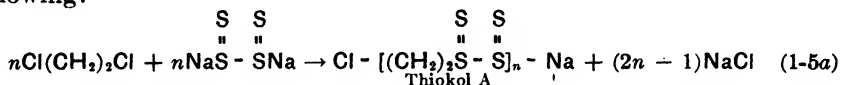
104. Addition Polymerization. Addition polymers usually form by the recurring interaction of unsaturated monomers containing a double

bond. In these polymers, the monomer is atomically identical with the mer and differs from it only in that the positions of certain bonds have shifted. Side products are not split out. The formation of polyvinyl chloride from vinyl chloride is a typical example.



(The chain ends of addition polymers are occupied, at least in part, by radicals derived from catalysts or impurities—Sec. 416.)

105. Condensation Polymerization. Condensation polymers form by the recurring reaction of monomers with the attendant splitting out of some simple molecule such as water, ammonia, sodium chloride, hydrogen chloride, or sodium bromide. With regard to these side products, the important point is that two different monomers each contribute part of the side-product molecule. In these reactions, the mer is not atomically identical with the monomer. Typical polycondensations are the following:



For Eq. (1-5c) the relation between monomer and mer is



106. Investigational Difficulties. It is obvious from the previous discussion that there is nothing intrinsically mysterious or unusual about the formation of huge molecules. It is to Carothers that we are particularly indebted for elucidating the inherent simplicity of the polymerization process. The student might well ask why our concepts of such a simple process were not clarified until the second decade of this century. The answer lies in the unusual properties of high polymers, which complicate their identification and investigation.

As ordinarily recovered from a reaction vessel, a high-polymer mass is tarry, oily, or resinous. Indeed, high polymers are often called *resins*.

Even when freed of impurities, which is in itself difficult, the molecules are not homogeneous, for during the polymerization process they do not grow to the same size. As a consequence, the product is devoid of precise physical constants and difficult if not impossible to purify, distil, or crystallize. There is no definite molecular weight, sorption of impurities is common, and no two successive batches are exactly alike. For these reasons, early-day chemists did the natural thing—they sighed and dumped the product down the drain, inscribing in their notebooks a statement to the effect that “a resinous mass of indefinite character was formed.”

The accumulation of precise information on high polymers therefore lagged. It was a slow, laborious process requiring the application of the very best of the older physicochemical techniques as well as the development of new ones, particularly x-ray diffraction analysis.

Staudinger pioneered in the subject, and Carothers, Flory, Huggins, Mark, Meyer, and others surmounted many of the main obstacles in a series of brilliant studies beginning in the 1920's. In the following decade, the foundations were laid for precise investigation of reaction mechanisms and properties so that it is now finally possible to select fairly accurately the reactants and conditions required to produce a high polymer with a given desired set of properties.

107. Degradation. Just as polymers may be built up, so also may they be torn down. *Degradation* may be defined as any process whereby the degree of polymerization is reduced. Degradation is called *depolymerization* if it is carried to the point where monomers are recovered.

The degradation of addition polymers may be effected by thermal or photochemical reversal of reaction (1-4); that of condensation polymers by a “hydrolytic” reversal of reaction (1-5). There is evidence that some polymers may be degraded by drastic mechanical working.

In processing natural polymers, we start with the high polymer ready made. As taken from the plant or animal, it is at its maximum degree of polymerization, and all processing to which it is subsequently subjected results in more or less degradation. Sometimes degradation is undesirable, and every precaution is taken to minimize it. At other times it is required, in which case techniques must be developed to control it lest it go too far or not far enough. Such controlled, deliberate degradation is analogous in aims and results to the cracking process employed in the petroleum industry.

108. Molecular Weights of High Polymers. It has already been mentioned that, when high polymers are synthesized, not all the molecules grow to the same size. And while natural high polymers are usually more uniform, there is still a considerable spread in the sizes and molecular

weights of individual molecules. Figure 1-2 shows the size-distribution curves for several polymers. (Molecular-weight distribution is discussed in Secs. 407 *ff.* and Sec. 614.)

It is well to bear in mind from the very beginning that a high-polymer mass, no matter how "pure," does not possess a molecular weight in the usual sense. Rather, it has an *average* molecular weight. Furthermore, when one refers to the degree of polymerization, one means the *average* degree of polymerization.

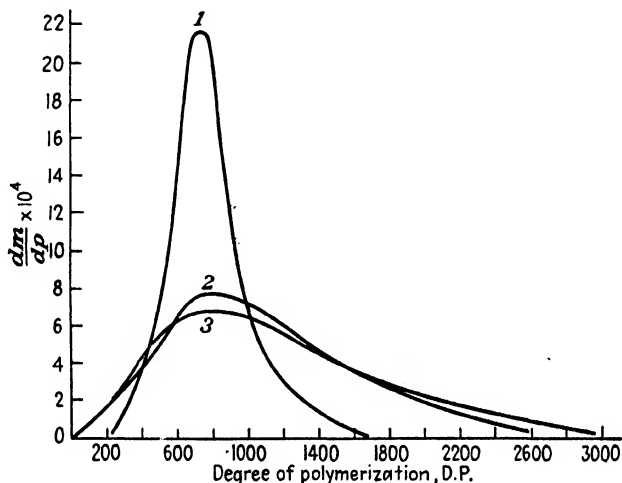


FIG. 1-2. Molecular-weight distribution; dm/dp is change of amount of material with degree of polymerization. Curve 1: cellulose nitrate, average D.P. = 800. Curve 2: polystyrene, average D.P. = 800. Curve 3: theoretical (Eq. 4-9), average D.P. = 800. [G. V. Schulz, *Z. physik. Chem.*, B **32**, 27 (1936); B **43**, 47 (1939).]

Size distribution may have significant effects upon physical and mechanical behavior. It is obvious that two specimens of a high-polymer material may have the same average molecular weight and yet differ considerably. One may consist of molecules of intermediate sizes with a narrow size distribution, the other of a mixture of very small and very large molecules.

Molecular weights are evaluated by measuring various properties. Colligative properties such as osmotic pressure and freezing-point depression are determined only by the total *number* of molecules; *i.e.*, each molecule affects the measured property to the same extent, regardless of its size, shape, or flexibility. Other properties such as viscosity, scattering of light, and rate of diffusion are influenced not only by the number of molecules but also by their size, shape, and flexibility.

When the molecular weight of a substance composed of simple molecules of identical size is measured via a property from each of these two

broad classes, the molecular-weight values can be identical since the factors of size, etc., are reduced to a constant. On the other hand, when applied to a typical high polymer in which there is a wide range of sizes, the molecular-weight values may be widely divergent. As a consequence, it has been found necessary in this field to establish several molecular-weight definitions, for example, the *number-average molecular weight* \bar{M}_n and the *weight-average molecular weight* \bar{M}_w .

$$\bar{M}_n = \frac{m}{n} = \frac{n_1 M_1 + n_2 M_2 + \cdots}{n_1 + n_2 + \cdots} = \sum \frac{n_i M_i}{n_i} = \sum N_i M_i \quad (1-6)$$

$$\bar{M}_w = \frac{m_1 M_1 + m_2 M_2 + \cdots}{m_1 + m_2 + \cdots} = w_1 M_1 + w_2 M_2 + \cdots = \sum w_i M_i \quad (1-7)$$

In the above relations, w is the total mass, n is the total number of moles of molecules of all sizes, and N_i and w_i are the mole and weight fractions, respectively, of that particular size of molecule whose molecular weight is M_i .

\bar{M}_n is the molecular weight in the usual classical sense. For a homogeneous material in which all the molecules are of one size, $\bar{M}_w = \bar{M}_n$ and $\bar{M}_w/\bar{M}_n = 1$. When, however, there is a size distribution, \bar{M}_w is greater than \bar{M}_n and the above ratio increases as size disparities grow broader. It is important to bear in mind that a number average imparts relatively greater significance to small molecules while a weight average emphasizes the effect and relative importance of large molecules.

This subject is dealt with at much greater length in Chap. 6, *e.g.*, in Sec. 617.

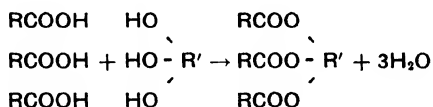
109. Functionality and Polymerization. When may polymerization occur? So far as any particular chemical reaction is concerned, a functional group is merely one which participates *in that reaction*. Functionality may be defined as the ability to form primary valence bonds. As will now be demonstrated, the number and kinds of functional groups present in any chosen set of reactants bear a simple and fundamental relationship to the types of product obtainable from the reaction, and if polymerization is to take place certain functionality requirements must be met. The esterification reaction will be used for illustrative purposes.

110. Mono-monofunctional Systems. The term *mono-monofunctional system* as here used implies a reaction between two molecular species, each possessing but one functional group. In an esterification, this would mean a monocarboxylic acid and a monohydric alcohol. Representing the nonfunctional (so far as esterification is concerned) parts of the reactants as R and R',



In this mono-monofunctional esterification, reaction ceases with the formation of the simple ester. The latter is no longer functional; it is incapable of further reaction *so far as esterification is concerned*. Polymerization does not result from such a combination of monomers.

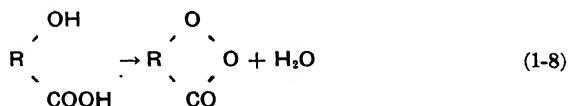
111. Mono-trifunctional Systems. Such a system involves the reaction of a monofunctional with a trifunctional compound. As an example, one may consider the reaction between a monocarboxylic acid and a trihydric alcohol.



The most extensive molecule that can result from such a combination is the monomeric triester.

Examination of a large number of cases permits the statement of a general principle. If two different reactants each contain only one kind of functional group and either one of the reactants is monofunctional, polymerization does not occur.

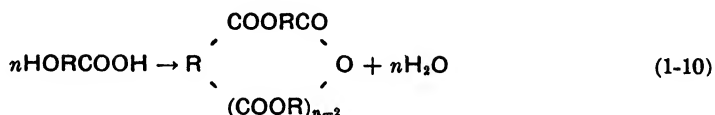
112. Bifunctional Systems. In this type of system, as the name implies, there is a single molecular species involved, but there are two functional groups of the proper kinds on the same molecule. So far as the esterification reaction is concerned, this means that the monomer is a hydroxycarboxylic acid. The situation is now quite different. Several possibilities present themselves. First, the functional groups might react *intramolecularly*, in which case the product is a cyclic monomer.



Second, the reaction might take place *intermolecularly*. If two of the original molecules interact, the reaction product is still bifunctional and hence immediately capable of further reaction. In other words, polymerization is a distinct possibility, since, offhand, there is no particular reason why the above process should not repeat itself over and over until very long molecules result. The product of the polymerization might be either of two types; it could be a long, open chain with functional groups at the ends, or the functional groups at the ends might eventually interact with one another, leading to the formation of a polymeric ring compound.

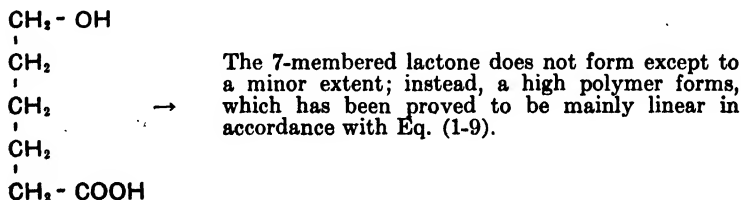
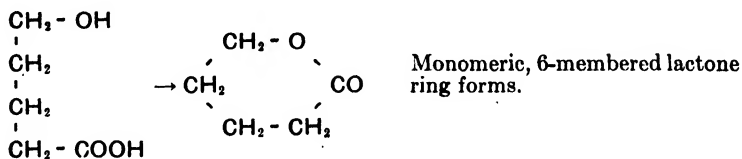
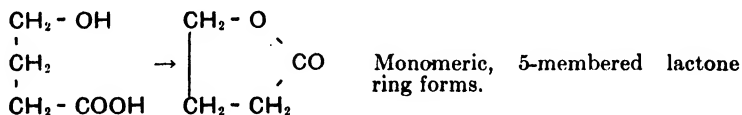


or



Equations (1-8) to (1-10) might be competing reactions leading to mixed yields.

Carothers and his coworkers studied bifunctional esterifications extensively and found that some led to cyclic monomeric products, others resulted in polymerization, while still others resulted in mixed yields. If the reaction product is a cyclic monomer, like small molecules in general it is relatively easy to recover, purify, and identify. Carothers found that bifunctional condensations which can lead to the formation of 5-membered or 6-membered rings almost invariably *do* result in such products. In other words, the reaction is intramolecular, proceeds in accordance with Eq. (1-8), and yields a cyclic monomer. Polymerization does not take place. On the other hand, he found that bifunctional condensations which would have to lead to the formation of larger than 6-membered rings by intramolecular reaction *do not* usually proceed in that way. Instead, high-polymer products result. For example, in the series of hydroxy acids represented by $\text{HO}(\text{CH}_2)_x\text{COOH}$, when x is 3 or 4, monomeric lactones form. When x is 5 or larger, condensation polymers form.

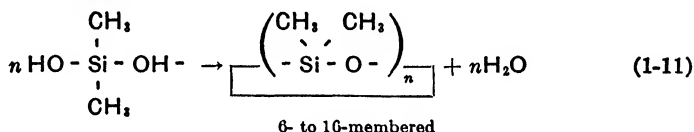


With hydroxy acids still longer than the hydroxycaproic acid shown above, the behavior is similar.

Similar results are obtained with compounds of the series $\text{H}_2\text{N}(\text{CH}_2)_x\text{Br}$

and also with the dicarboxylic acids represented by the general formula $\text{HOOC}(\text{CH}_2)_x\text{COOH}$. In the latter series, when x is 2 or 3 (succinic or glutaric acid), monomeric cyclic anhydrides form. Beginning with adipic acid where x is 4, polymeric products result. Not that adipic anhydride cannot be synthesized; quite to the contrary, it may be made by any of several methods. The point is that it cannot be prepared in satisfactory yield via bifunctional condensation.

The rules stated above are not hard and fast. In the amino acid series, $\text{H}_2\text{N}(\text{CH}_2)_x\text{COOH}$, in the borderline case where x is 5, a 30 per cent yield of 7-membered cyclic monomeric lactam is obtained together with 70 per cent of linear polyamide. However, when x is 6, almost the entire yield is linear high polymer. More striking is the case of the silicone polymers. For example, the hydrolysis of dichlorodimethylsilane may, under certain conditions, result in mixed yields of cyclics containing 6 to 16 atoms in the ring. Reaction (2-1), page 39, is followed by



When polymerization does take place, average molecular weights in the thousands are obtained. The question is whether the product is a long open chain in accordance with Eq. (1-9) or a huge closed ring in accordance with Eq. (1-10). The fact that it is difficult to obtain even 7-membered rings is of itself a strong indication favoring reaction (1-9). One might think that the matter could be very readily settled by establishing the presence of functional terminal groups by a simple analysis, but a consideration of the nature and behavior of high polymers indicates the difficulties involved; *e.g.*, the functional groups are only a very small fraction of the total weight of the molecule, and hence stoichiometric relationships are difficult to establish; powerful adsorption phenomena are likely to take place in high-polymer products; impurities are very difficult to remove, since solution, distillation, and crystallization are often impossible. However, what clear-cut evidence has been gained from cases that do lend themselves to exact study points very strongly toward reaction (1-9), as may be gathered from the discussion of the bi-bifunctional reaction immediately following. It might be well in passing to point out that, since an olefinic bond is essentially a bifunctional structure, addition polymerizations such as Eq. (1-4) are bifunctional reactions.

113. Bi-bifunctional Systems. In a bi-bifunctional system, reaction takes place between two different species of bifunctional monomers. For esterification this would involve a glycol and a dicarboxylic acid.



That this type of reaction is very similar to the bifunctional is evident from a consideration of the nature of the dimer, HOR'OOOCR'COOH . Reaction between such dimers is typically bifunctional. However, it is important to note that even if R and R' are identical, the linear polymers resulting from reactions (1-9) and (1-12) are still different in structure. In the first case, the ester groups occur "back to front"; in the second case, they are "back to back." Such structural variations may result in important differences in physical properties.

TABLE 1-2. PROPERTIES OF POLYESTERS

Polyester	Mer	Analyses				M.W. values	Melting point, deg C
		Found, %		Calculated for mer, %			
		C	H	C	H		
Ethylene malonate	$\text{—O(CH}_2\text{)}_2\text{OC(=O)CH}_2\text{C(=O)—}$	46.46	4.84	46.15	4.65	2,300–3,500	Liquid
Ethylene succinate	$\text{—O(CH}_2\text{)}_2\text{OC(=O)(CH}_2\text{)}_2\text{C(=O)—}$	49.82	5.61	49.97	5.58	2,300–3,500	108
Ethylene adipate	$\text{—O(CH}_2\text{)}_2\text{OC(=O)(CH}_2\text{)}_4\text{C(=O)—}$	55.28	7.06	55.78	7.03	2,700–3,900	50
Hexamethylene succinate	$\text{—O(CH}_2\text{)}_6\text{OC(=O)(CH}_2\text{)}_2\text{C(=O)—}$	59.32	7.92	59.97	8.05	3,200–3,500	57
Hexamethylene adipate	$\text{—O(CH}_2\text{)}_6\text{OC(=O)(CH}_2\text{)}_4\text{C(=O)—}$	62.57	8.86	63.10	8.85	3,300	56
Decamethylene succinate	$\text{—O(CH}_2\text{)}_{10}\text{OC(=O)(CH}_2\text{)}_2\text{C(=O)—}$	64.67	9.28	65.57	9.45	3,200–3,500	68
Decamethylene adipate	$\text{—O(CH}_2\text{)}_{10}\text{OC(=O)(CH}_2\text{)}_4\text{C(=O)—}$	67.27	9.94	67.56	9.92	3,200–3,300	77
Decamethylene sebacate	$\text{—O(CH}_2\text{)}_{10}\text{OC(=O)(CH}_2\text{)}_8\text{C(=O)—}$	70.76	10.73	70.53	10.67	3,000	74

Carothers and his coworkers synthesized a whole series of polyesters, ranging from polyethylene malonate to polydecamethylene sebacate, using bi-bifunctional combinations. Some of the properties are listed in Table 1-2. When ethylene glycol and succinic acid were condensed, no appreciable amount of cyclic monomers formed. The product was a typical linear polyester, and the reaction could be carried out in the presence of either a small excess of glycol or a small excess of succinic acid. In both cases, the products were of such crystallizability and purity that the presence of terminal groups could be established. In the first instance, they proved to be alcohol groups; in the second, they were carboxyl groups. Furthermore, the molecular weights of the acidic esters as determined by titration of the end groups agreed very well with those determined by other methods as shown in Table 1-3. This again

TABLE 1-3. ACIDIC ETHYLENE SUCCINATES
 $\text{HOOC}(\text{CH}_2)_2\text{CO}-[\text{O}(\text{CH}_2)_2\text{OOC}(\text{CH}_2)_2\text{CO}]_x-\text{OH}$

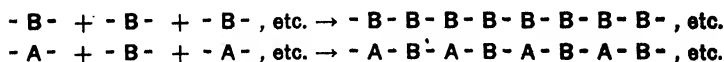
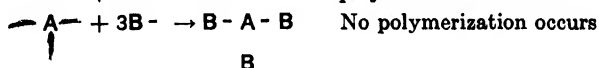
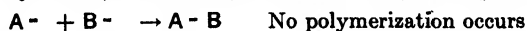
<i>x</i>	Acid			Sodium salt	
	Melting point, deg C	M.W. calculated from neutralization equivalent	M.W. found by ebullioscopy	Melting point, deg C	M.W. calculated from sodium content
6	73	1,020	1,070	91	1,030
9	82	1,340	1,380	97	1,460
12	90	1,800	1,580	100	2,010
23	98	3,400	3,110	109	3,740

CAROTHERS, W. H., *Chem. Revs.*, **8**, 353 (1931).

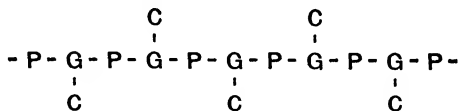
may be taken as good evidence that, in the main, polymeric products of bifunctional and bi-bifunctional esterifications are long open chains rather than huge rings.

114. Polyfunctional Systems. For the sake of greater ease of presentation, the following symbols will now be adopted, in which a functional group is represented merely by a bond line. Thus, A— and B— are monofunctional molecules, —A— and —B— are bifunctional, and —A— and —B— are trifunctional.

With these symbols, what has gone before may be expressed as follows:



The important difference between these chains and the ones formed from an ordinary bi-bifunctional combination is that they are multifunctional. Heating them with a monofunctional carboxylic acid such as C— reduces them to nonfunctional linear chains.

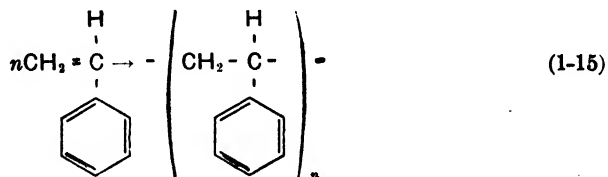


This is an application of the important technique called *blocking*. On the other hand, a mixture of the functional chains of Eq. (1-14) with additional amounts of bifunctional acid such as —P— constitutes a polyfunctional system, and reaction between them results in cross-linkage such as obtained directly in Eq. (1-13). The important point to note is that the system can be brought to a condition of linear functional polymers by a first addition of —P— and later converted to a space polymer by reaction with a second portion (excess) of —P—.

In summarizing, it is evident that a polyfunctional system of reactants is more versatile than other systems in that linear nonfunctional, linear functional, and space polymers with varying degrees of cross-linkage may all be produced depending upon the manipulation of relative concentrations of the reactants, temperature, catalyst, time, etc., and the use or nonuse of blocking agents.

Since, roughly speaking, linear-polymer masses are soluble, fusible, and moldable in contrast with space polymers, which are insoluble, infusible, and nonmoldable, the importance of cross-linkage and the manipulability of polyfunctional systems can scarcely be overemphasized. Table 1-4 contains several important examples of such systems.

115. Copolymerization and Heteropolymerization. The polymerization of two or more units, each of which is independently capable of polymerization, into the same chains is the process called *copolymerization*. For example, styrene can polymerize into polystyrene,



and butadiene polymerizes per se to form polybutadiene by the diene polymerization reaction,

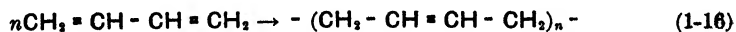
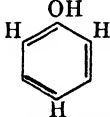
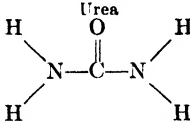
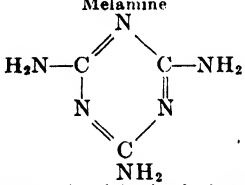
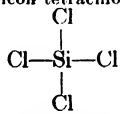
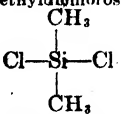
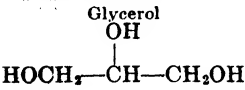
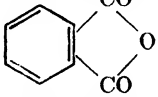
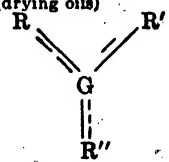
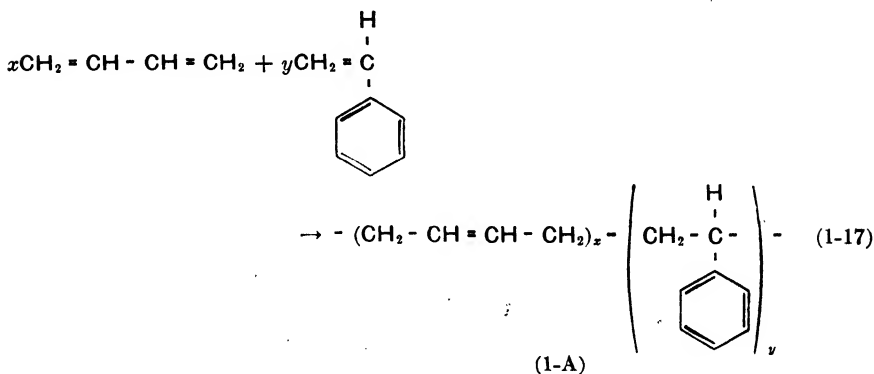


TABLE 1-4. SOME IMPORTANT POLYFUNCTIONAL SYSTEMS

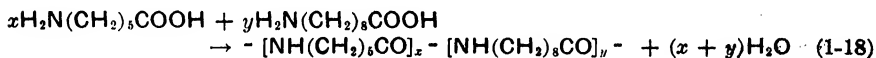
Reactants		Product
Natural (Hevea) rubber $\left(\text{CH}_2 - \underset{\text{Multifunctional}}{\underset{\text{CH}_3}{\text{C}}} = \text{CH} - \text{CH}_2 \right)_n -$	Sulfur S Bifunctional	Vulcanized rubber
Phenol 	Formaldehyde (methylene glycol) $\text{HO}-\text{CH}_2-\text{OH}$ Bifunctional	Phenol-formaldehyde resins
Trifunctional (ortho and parahydrogens)	Formaldehyde	
Urea 	$\text{HO}-\text{CH}_2-\text{OH}$ Bifunctional	Urea-formaldehyde resins
Tetrafunctional (amine hydrogens)	Formaldehyde	
Melamine 	$\text{HO}-\text{CH}_2-\text{OH}$ Bifunctional	Melamine-formaldehyde resins
Hexafunctional (amine hydrogens)	Silicon tetrachloride 	
Dimethyldichlorosilane 	Tetrafunctional	Silicones
NOTE: Chlorines converted to hydroxyls by hydrolysis. Polycondensation follows		
Glycerol 	Phthalic anhydride 	Glycerol-phthalic acid resins
Trifunctional	Bifunctional	
Conjugated unsaturated triglyceryl esters (drying oils) 	+ etc.	Dried varnish film
NOTE: — represents a double bond along a hydrocarbon chain		

By mixing monomeric butadiene and styrene and establishing proper reaction conditions, a butadiene-styrene copolymer is obtained.



This copolymer is buta S (buna S), a synthetic rubber of critical importance during the Second World War.

Similarly, 5-aminocaproic acid and 8-aminononanoic acid are independently capable of polymerizing to polyamides (nylons) via bifunctional condensation. A mixture of the monomers dissolved in a solvent copolymerizes under suitable conditions.

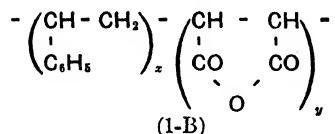


By varying both the kinds and relative amounts of two monomers used in a copolymerization a whole series of products may be manufactured with a considerable spread in physical and mechanical properties. The range of useful products may be still further extended by copolymerizing three, four, or even more monomeric species, often of radically different structures and chemical composition. From a relatively small number of monomeric raw materials it is thus possible to make a tremendous number of polymeric products. In a sense, copolymerization does for high polymers what alloying does for metals. Of the synthetic high polymers used today, by far the greater number are copolymers.

So far as is known, the structural units of a copolymer occur at irregular, random intervals along the chains, and it is evident from Eq. (1-17) that the introduction of styrene units into the buta S chain gives the molecules a "bumpy," irregular contour. In other words, copolymerization reduces the molecular symmetry, a point whose basic significance will become evident later. Copolymers are sometimes called *interpolymers*.

The term *heteropolymerization* is sometimes applied to the ~~special~~

case of copolymerization where one of two units or monomers that will copolymerize is incapable of polymerization per se. Thus, styrene readily forms polystyrene, but maleic anhydride, although possessing double bonds, does not combine with itself to form a polymer. Nevertheless, styrene and maleic anhydride copolymerize to form the *heteropolymer* shown.

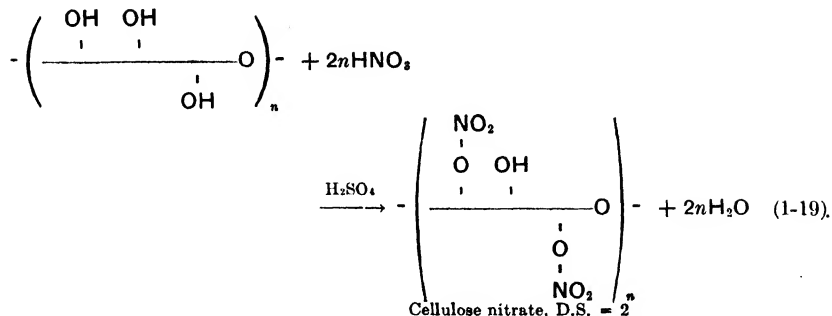


116. Chemical Modification of High Polymers.—A synthetic polymer of a desired chemical composition is produced by first synthesizing the appropriate monomers and then polymerizing them in proper combinations and amounts. Seldom are chemical transformations performed on the synthetic polymer after it has been polymerized. On the other hand, natural polymers come ready-made from various biological and geological processes. Often their properties do not suit us, in which case we modify them, usually by chemical transformation. A few examples follow.

The mer of natural rubber (Table 1-1) contains a double bond. This functional group has a great virtue in that it enables us to vulcanize the rubber with sulfur. However, the double bond is also a source of weakness in that it leaves the rubber open to the deteriorating actions of heat, light and oxygen. By the addition of chlorine or of hydrogen chloride, chlorinated rubber or rubber hydrochloride, two chemically stable polymeric derivatives excellent for certain special applications, can be made.

Wool is a complex polyamide (protein) with cystine cross-links connecting the main chains. By chemically rupturing these cross-links and rebuilding them in modified form, the resistance of wool to shrinkage and attack by moths and strong chemicals is notably enhanced.

But perhaps most important of all are the chemical modifications performed on cellulose. As originally recovered from plants, the molecules are very long, the D.P. probably exceeding 3,000. From Table 1-1 it is seen that each cellulose mer has three alcohol groups (strongly polar). For these and other reasons, cellulose is insoluble, infusible, and nonmoldable in spite of its linear-polymeric structure. Soluble, moldable derivatives may be made by substituting ester, ether, or other groups for part or all of the original alcohol groups. Thus, representing the cellulose mer by a symbol easy to write, the conversion to a cellulose nitrate with two-thirds of the alcohol groups substituted by nitrate groups is shown below:



The *degree of substitution*, often represented by the abbreviation D.S., is defined as the average number of alcohol groups per mer that have been replaced. Accordingly, the D.S. may have any value between 0 and 3.0, the former corresponding to 0 and the latter to 100 per cent substitution. It is important to note that *partial substitution*, such as that shown in Eq. (1-19), reduces the molecular symmetry and otherwise produces effects similar to those of copolymerization. Only through substitution is it possible to make cellulose products suitable for the manufacture of rayons, cellophane, photographic film, and binders for plastics and surface coatings. It should be noted that some degradation always accompanies substitution (Sec. 107) and affects the properties of the final product.

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 MARVEL, C. S., and E. C. HORNING, Chap. 8 in "Organic Chemistry," H. GILMAN, editor, John Wiley & Sons, Inc., New York.

See also Appendix A.

PARTICULAR TOPICS

See references accompanying tables and figures of this chapter.

CHAPTER 2

MOLECULAR FORCES

200. In dealing with masses of molecules one must consider not only the *intramolecular* forces which hold one atom to another within a molecule but also the *intermolecular* forces by which the molecules as separate entities are held to one another. The former are strong and are called *primary valence forces*; the latter are weaker and are commonly termed *secondary valence forces* or *intermolecular attractive forces*. In this text the term *bonding* will be used to describe primary valence forces and *bridging* to describe secondary intermolecular attractions.

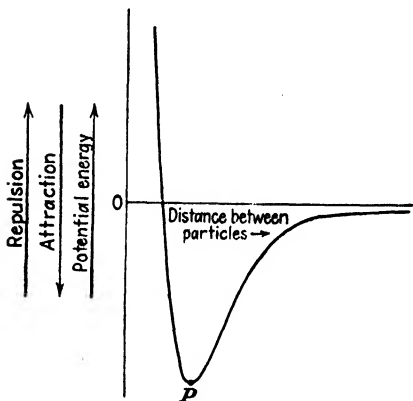


FIG. 2-1. Potential energy as a function of distance for a system of two particles.

These are termed the *valence electrons*, while the remainder of the atom is called the *core*.

The quantum theory has been applied with great success to atomic structure and has enabled the calculation of the attractive forces between atoms. The relationships are usually expressed by a potential curve. Any system of two particles, whether they be atoms or not, may be considered to possess energy by virtue of a force that the particles exert on one another at varying distances apart. This force may be considered as the algebraic sum of an attractive force and a repulsive force. The general form of the curve is shown in Fig. 2-1. Let us say that the potential energy is zero when the two particles are infinitely separated. As they approach each other by attraction; the potential energy decreases

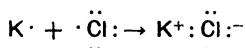
✓ PRIMARY VALENCE FORCES

201. The mass and positive charge of the atom are concentrated in a very small nucleus, which is surrounded by concentric "shells" of electrons at a relatively large distance from the nucleus. The electrons in the outermost shells are the least firmly bound. Chemical reaction between atoms is confined to the electrons in the outermost groups (the ones of highest quantum

until at point *P* it has reached a minimum. At *P* the forces of attraction and repulsion are equal, and this point may be regarded as the position of normal approach. Any attempt to move the particles still closer together must be done against a rapidly increasing repulsive force, and the potential energy again rises. If the particles involved happen to be the atoms of a diatomic molecule, the distance of normal approach is found to be about 1 or 2 Å. The precise shape of the curve, its coordinates, and its equation vary with and can be calculated from the particular valence forces acting. The repulsion on close approach arises from the mutual effect of the electron shells of the atoms upon one another.

The primary valence forces binding one atom to another in a molecule have been found to be of different kinds, as will now be described.

202. The Ionic Bond. The most stable configuration of the outer electrons of all the elements except the very light ones, such as hydrogen, is a shell of eight. Atoms of many elements attain an outer group of eight electrons, and with it greater stability, by exchanging electrons with other atoms. Thus the following scheme represents the formation of potassium chloride:

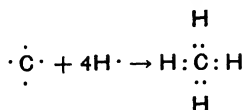


The two atoms are then held together by electrostatic forces. Such a linkage is termed an *ionic bond*. An ionic bond is a chemical bond between atoms, in which one or more electrons are given up by the electropositive element or group and transferred to the electronegative one, the resultant ionic structures being held together by the mutual attraction of opposite electric charges. The oppositely charged ionic parts of this polar molecule can attract similar molecules and result in the building of an entire salt crystal all the units of which are held together by the ionic primary valence bond. Consequently, the entire crystal is in a sense one molecule—in this case, a polymer representable as $(\text{KCl})_n$.

The distance of approach of the ionic structures is limited by the repulsion of the electron shells. The potential equation contains terms for the Coulomb's law attraction, for electron repulsion, and for an attraction due to the deformation of the electron shells of the anions by the positive charges on the cations.

The ionic bond has also been called the *polar bond*, the *electrovalent bond*, and the *heteropolar linkage*.

203. The Covalent Bond. Many chemical compounds, particularly the organic, are nonionic in character. The structure of methane, a molecule typical of this class, is conveniently illustrated by the following graphical notation:



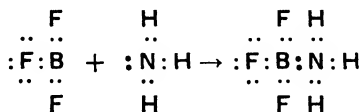
In this type of linkage, which is termed nonpolar, the atoms attain stable shells of eight, not by losing or gaining electrons, but by "sharing" electrons with an adjacent atom. More specifically, a *covalent bond* is a chemical bond between atoms or groups in which one or more pairs of electrons are shared, the atoms or groups being held together by the stable configuration resulting from the sharing. Offhand, there would seem to be no field around the methane molecule such as exists about the ionic potassium chloride molecule. Hence it might be concluded that a methane molecule could not exert an attraction on others around it. This is not quite so. Even about such structures there is a residual field, albeit a weak one, which leads to intermolecular attractions.

The concepts of electron transfer and electron sharing have proved to be a fruitful contribution to valence theory, and the distinction between the above two types of bonds is fundamental.

The potential curve for the covalent bond was first calculated by the application of the Schrodinger equation of quantum mechanics, and great success has been attained both in calculating valence forces and accounting for many fundamental features of molecular structure such as the existence of spatially defined valence directions (bond angles), the free rotation about a single bond, and the rigidity of the double bond.

The covalent bond is sometimes also known as the *nonpolar bond* or *homopolar linkage*.

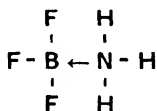
✓ **204. The Coordinate Bond.** Still another type of bond occurs—the *coordinate*—whose existence was postulated by Werner to explain the properties of certain compounds. The octet theory also successfully accounts for it. It is perhaps most frequently met with in molecular compounds such as hydrates and ammoniates. An interesting example is afforded in the formation of the ammoniate of boron trifluoride.



In the above notation, the electrons of particular interest are shown as heavier dots. As in the case of the covalent bond, a stable structure of eight is reached by the sharing of a pair of electrons, but in this case *both* the electrons of the shared pair are supplied by the one (nitrogen) atom. The electron pair being furnished solely by the one atom, this atom in effect "loses" one electron (one-half of the shared pair). The donor

(nitrogen) therefore becomes positive and the acceptor (boron) negative. The coordinate bond partakes of some of the properties of both the ionic and covalent bonds. It may be thought of as a double bond made up of one ionic and one covalent bond and as a consequence has also been termed the *semipolar bond*.

The coordinate bond is frequently represented by an arrow pointing from the electron donor to the acceptor.



The three types of primary bonds thus far described are those commonly encountered in inorganic and organic molecules. They have values of 20 to 200 kcal per g-mole.

✓ **205. Resonance.** One outgrowth of quantum mechanics, the concept of resonance, has proved extremely fruitful in explaining various chemical phenomena. In barest outline it is as follows: If, in accordance with certain rules stated below, it is possible to write down two or more plausible electronic structures for a molecule, then no one of these structures by itself may be considered to represent the normal state of the molecule; rather, the molecule behaves as though it were a hybrid (*but not a mixture*) of all the structures. Furthermore, the molecule is more stable than it would be if it had any single one of the postulated structures, even the form of lowest energy level. The molecule is said to be *resonating* among the various structures and the energy stabilizing it is called the *resonance energy*.

The main conditions imposed on the writing of resonating structures are that they correspond to nearly the same energy, conform to a single atomic (nuclear) configuration, and possess the same number of unpaired electrons.

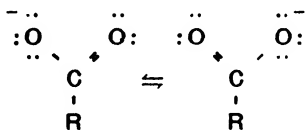
The resonance effect depends on the relative energies of the resonating structures. Thus, if two structures meeting the above rules may be written and they have the same energy, the molecule resonates equally between them and the resonance energy is large. By contrast, if the first of the two structures is considerably less stable than the second, its contribution is relatively small and resonance results in a molecule only slightly more stable than the second.

Following the rules stated above, for a molecule of hydrogen it is possible to write only one electronic structure, $\text{H}:\text{H}$, that is, a normal covalent bond between two hydrogen atoms. But for HCl one may write two reasonable structures, $\text{H}:\ddot{\text{Cl}}:$ and $\text{H}^+ : \ddot{\text{Cl}}^-$, the first corre-

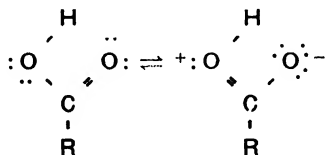
sponding to a normal covalent, the second to an ionic bond. Since chlorine is electronegative with respect to hydrogen, it may be expected that the ionic structure will be not too greatly different from the covalent structure in energy, although less stable. The two structures satisfy the conditions for resonance, and it is deduced accordingly (1) that the bond between the hydrogen and the chlorine in the normal HCl molecule is a partly covalent, partly ionic hybrid with covalent character predominant and (2) that, as a result of resonance, this bond is stronger than either the normal covalent or the ionic.

The above example serves to demonstrate the fruitfulness of the resonance concept. For one thing, it affords an explanation for the fact that covalent bonds between certain unlike atoms (HCl, HBr, etc.) are more stable than those between like atoms (Cl_2 , Br_2 , etc.). For another, it implies that a single bond may vary anywhere in character between the ionic extreme and the covalent extreme and that the ionic and covalent bonds discussed in Secs. 202 and 203 are merely main *types* between which there are no sharp lines of demarcation. This turns out to be so.

As another illustration, it may be postulated that carboxylic ions resonate between



Since these are equivalent structures, it is deduced that the resonance energy will be comparatively large. For the corresponding carboxylic acid, two structures may also be written,

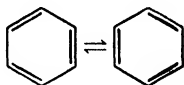


but these are not equivalent. The stabilizing effect of this resonance is thus less than that in the carboxylic ion. It is deduced accordingly that the greater stability of the ion due to greater resonance energy aids in detaching the proton from the acid, thereby helping to account for the acidic properties.

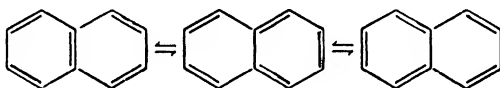
Thermochemical measurements show that, if one considers only molecules for each of which only a single valence-bond structure may be drawn (*i.e.*, nonresonating molecules), one may calculate accurately the energy of formation from the atoms from a table of constant energy values for

individual bonds. But on applying such a table of bond energy values to resonating molecules it is found that the energy of formation is invariably greater than the calculated value, *i.e.*, that the molecules are actually more stable than expected. By taking the difference between the observed energy of formation and the calculated, one obtains for each resonating molecule an empirical value for its resonance energy.

For benzene, several resonating structures may be drawn, but by far the most important are



Since these represent identical energy levels, it is deduced from resonance concepts that the resonance energy is large and the molecule consequently stable and that all the aromatic carbon-to-carbon bonds are equivalent. This is in excellent agreement with fact. X-ray diffraction and other measurements show that all the bonds are of an identical length intermediate between that of C—C and C=C bonds. For naphthalene, three predominantly important structures may be drawn.



These contribute about equally to the resonating structure and account for the aromatic character similar to benzene. It is an important fact that for benzene and naphthalene the empirical resonance energy values in kilogram-calories per gram mole are 39.4 and 74.6, respectively.

Resonance concepts have contributed notably to the elucidation of acid strengths, stability of free radicals, the directive effects of substituent groups, the color of dyes, and other important phenomena.

206. The Metallic Bond. Until comparatively recently, very little was known about the bonding forces acting in metals. That these forces are often greater than those acting in other materials is evident from the high tensile strengths and melting points possessed by some metals. That the metallic bond is different from those thus far discussed is obvious from the fact that it cannot be depicted in harmony with the laws of ionic and covalent bonding. In a metal, there is such a general dearth of valence electrons that the concept of the formation of stable electronic configurations by electron transfer or electron pair sharing is unfruitful.

When two metallic atoms approach one another, their electrons form a valence bond that, owing to the small number of valence electrons

available, is far short of a complete shell. Accordingly, on the approach of another metallic atom, this, too, is added; and as more and more atoms enter the aggregate, this effect continues, the electrons forming bonds that are essentially covalent in nature but spread throughout the entire group of atoms, holding them all together. The distinguishing features of the metallic bond as compared with the covalent bond are (1) that there is no saturation of valence, so that any number of atoms can be held together, forming a crystal rather than a finite molecule; (2) that the bond is not directional. The lack of direction in the bonding forces results in the characteristic properties of ductility, malleability, and cold working in this manner: the individual atoms in the lattice may be moved past one another without suffering any essential change in environment, so that large distortions do not weaken the lattice.

The different number of valence electrons in the various metals produces different degrees of bonding. Thus, the alkali metals have only one outer electron per atom. This must be shared with eight neighbors. The resulting bonding is weak, the melting point is low, and the metal is weak in tension and has a cheeselike softness. The alkaline earths have two outer electrons to be shared. This results in more extensive bonding, greater strength, and greater hardness. Succeeding elements in the series have still more electrons, which increase the tightness of binding and produce still stronger structures, attaining very high values in many elements such as iron, nickel, and cobalt. Beyond a certain point, however, metallic elements that have many electrons available for bonding tend to form localized valence bonds, resulting in brittle structures, as in arsenic, antimony, and bismuth.

The most conspicuous property of metals is electrical conductivity. This is also a consequence of a small number of valence electrons relatively distant from the balance of the atom. These electrons are readily removed; *i.e.*, the metallic atoms in the gaseous state have low ionization potentials, and the sharing of the valence electrons with many neighboring atoms loosens the electrons and permits free motion. The structure is one of electropositive ions immersed in a cloud of mobile electrons.

207. Primary Valence Bond Values. From measurements of heat capacities, dissociation energies, heats of combustion, and spectroscopic data, coupled with crystallographic, x-ray-diffraction, electron-diffraction, and polarization measurements as well as still other data, there has been built up a detailed body of knowledge, not only of the strengths of primary valence bonds and the angles that these bonds make with one another, but also of the sizes and locations of individual atoms in crystals. That is, the study of bond energies overlaps that of molecular structure. Properties of some primary valence bonds are given in Tables 2-1 and 2-2.

TABLE 2-1. PROPERTIES OF SOME PRIMARY VALENCE BONDS

Linkage	Bond length, Å	Dissociation energy, kcal/g mole
C—C aliphatic	1.52–1.55	59–70
C—C aromatic	1.39–1.42	
C—C aliphatic-aromatic	1.48–1.50	
C=C	1.30–1.34	100–125
C≡C	1.19–1.22	123–162
C—H	1.08–1.12	87–94
C—Cl	1.69–1.76	66
C—N	1.38–1.47	49–60
C=N	1.31	94–125
C≡N	1.17	150–185
C—O	1.46	70–75
C=O	1.13–1.28	142–166
C=S	1.54–1.56	103
N—O	1.15	57
N—H	1.02–1.06	84–97
O—H	0.96–1.02	101–110
O—Si	1.17	89
Na—Cl	2.82	183
K—Cl	3.14	165
K—K	4.62	16.5
Cu—Cu	2.55	81

The bond lengths quoted above are those usually encountered. In molecules in which extraordinary distortions are produced by large side groups, cyclic structures, etc., bond lengths may fall outside the ranges quoted and differ from the average values by as much as 25 per cent.

Data from several sources, notably

GILMAN, H., editor, "Organic Chemistry," John Wiley & Sons, Inc., New York, 1943.

PAULING, L., "Nature of the Chemical Bond," Cornell University Press, Ithaca, New York, 1939.

TABLE 2-2. BOND ANGLES

Substance	Method	Bond angle	Experimental value
CH ₃ —CH ₂ —CH ₂	Electron diffraction	C—C—C	111°30'
C ₆ H ₁₂ N ₄	Crystal structure and electron diffraction	N—C—N	110°
N(CH ₃) ₃	Electron diffraction	C—N—C	108°
H ₂ O	Spectroscopy	H—O—H	105°
(CH ₃) ₂ O	Electron diffraction	C—O—C	111°
Cl—CH ₂ —Cl	Spectroscopy	Cl—C—Cl	108°
C ₆ H ₅ —S—C ₆ H ₅	Polarization	C—S—C	113°
$\begin{array}{c} \text{C} \\ \diagup \\ \text{X}=\text{C} \\ \diagdown \\ \text{C} \end{array}$	X-ray diffraction and others	X=C—C	~125°

Data from several sources, notably

PAULING, L., "Nature of the Chemical Bond," Cornell University Press, Ithaca, New York, 1939.

SECONDARY VALENCE FORCES

208. After two or more atoms have combined to form a molecule, this still does not mean that all the forces between the electrons and the nuclei have been neutralized. The molecule is still able to exert a force of attraction on others around it. For the existence of such intermolecular attractive forces there are many evidences, one of which need be mentioned here.

1. In order to convert a liquid to vapor, considerable energy, the latent heat of vaporization, must be supplied.

2. In the absence of such forces, all compounds composed of electrically neutral molecules would be gases at all temperatures, which is not the case.

3. Gases would not exhibit deviations from the perfect gas law.

209. Magnitude of Secondary Valence Forces. The potential curve for the forces acting between two molecules is similar in form to that for two atoms within a molecule, but the forces involved are of lower magnitude. These intermolecular, or secondary valence, forces are in most cases of the order of 0.5 to 5 kcal per g mole. Furthermore, the distance of normal approach lies in most cases between 3 and 5 Å (as compared with 1 to 2 Å in the case of primary valence forces).

210. Nature of Secondary Valence Forces. Secondary valence forces are due to residual fields left about the molecule as a whole after two or more atoms have combined through primary bonds to form the molecule itself. Since the secondary valence forces are inherently weak, in small molecules they are overshadowed by the primary forces; but when molecules grow very large, these forces assume spectacular importance. Other names that have been applied to them are *residual valence forces*, *van der Waals forces*, *intermolecular forces of attraction*, and *intermolecular cohesive forces*. In the liquid and solid states, the term *internal pressure* is also applied. So far as the subject has been developed up to this time, secondary valence forces acting between molecules may be attributed to the presence of electric moments in the individual molecules. If, in an electrical system, the center of action of the positive charges coincides with the center of action of the negative charges, the system as a whole has no dipole moment. Consider two different arrangements of equal and opposite charges at the corners of a square as shown in Fig. 2-2. In Fig. 2-2a, the centers of action of both the positive and negative charges are at point *O*. Such a system has a dipole moment of zero. In Fig. 2-2b, the center of action of the positive charges is at *L*, while that of the negative charges is at *M*. Electrically it may be regarded as equivalent to a rod of length *s*, negatively charged at one end, in this case with a charge

of $2e$, and with an equal positive charge at the other. The *dipole moment* of this system is $2es$ and is permanent.

The system represented in Fig. 2-2a will be devoid of a dipole moment only so long as the charges hold their relative positions. If the system should suffer distortion or displacement of the charges due, for example, to the influence of an outside field, an *induced moment* may be set up that will vary with the intensity of the field and will disappear if the field is removed and the charges return to their original positions.

In molecules, the positive charges are concentrated in the nuclei, and the negative charges reside in the electrons. Various ways in which electric moments may be established in the molecule and thus may result in intermolecular attractions will now be discussed.

211. Polar and Nonpolar Structures.

A molecule or part of a molecule is termed *polar* if it possesses a permanent dipole moment. The dipole moment is a vector quantity having magnitude, sign, and direction. If, therefore, a molecule contains two or more polar bonds, particularly in close proximity, they exert an influence on one another such that the over-all moment is the resultant of the individual moments and may be positive, negative, or zero. In other words, the architectural arrangement of the bonds, as well as their inherent polarity, contributes to the overall polarity. The dipole moment and dielectric constant are both measures of polarity, although neither may be adopted as an infallible quantitative index to the behavior of the molecule. (See Sec. 1004 for the relationship between these quantities and for the method of determination of dipole moments.)

When two parts of a molecule are joined by the ionic bond, there is a strong, permanent moment at the bond traceable to the electron transfer that has taken place. The ionic bond is thus always strongly polar.

In the formation of the covalent bond, no electron transfer occurs. Consequently, this bond is inherently of low polarity. But molecules held together by covalent bonds may nevertheless be polar. The architecture of the molecule, *i.e.*, the location of the positively charged nuclei, is important. Consider the water molecule. It is triatomic, and the atoms are held together by covalent bonds. If the atomic nuclei lay

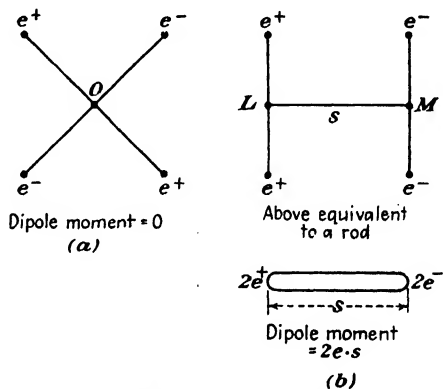


FIG. 2-2. Dipole moment and distribution of charge.

in a straight line with the hydrogen atoms symmetrically disposed on opposite sides of the oxygen atom, that is, $\text{H}-\text{O}-\text{H}$, the dipole moment would be expected to be zero. The fact is, however, that water has a permanent dipole moment and a high dielectric constant. From this it is deduced that there is a hook in the molecule and that the valence bonds

TABLE 2-3. POLAR PROPERTIES OF ORGANIC COMPOUNDS
(Dielectric constants are those of liquid at or near 20 C)

Compound	Dipole moment, debyes	Dielectric constant	Type of compound	Dipole moment, debyes (average values)
$n\text{-C}_6\text{H}_{14}$	0.0	1.87	n -Hydrocarbons	0.0
C_6H_6	0.0	2.29	Alkyl chlorides	2.0
			n -Alcohols	1.7
CH_4	0.0		Ethers	1.2
CH_3Cl	2.0		Aldehydes	2.5
CH_2Cl_2	1.6		Ketones	2.7
CHCl_3	1.1	5.05	n -Acids, carboxylic (except formic)	0.7
CCl_4	0.0	2.24	Amines:	
			Primary	1.3
HOH	1.84	80	Secondary	1.0
CH_3OH	1.68	34	Tertiary	0.8
CH_3NH_2	1.3	10	Aminoacid esters	2.1
CH_3NO_2	3.0	39	Amides	3.6
			Cyanides	3.4
HOH	1.84	80	Nitroparaffins	3.1
$\text{C}_2\text{H}_5\text{OH}$	1.70	26	Nitrites	2.2
$\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$	1.15	4.3	Nitrates	2.9
$\text{C}_2\text{H}_5\text{NH}_2$	1.3	6.3	Mercaptans	1.3
$\text{CH}_2\text{OHCH}_2\text{OH}$	2.3	41	Sulfides	1.5
$\text{CH}_2\text{NH}_2\text{CH}_2\text{NH}_2$	1.9	16		
CH_3CHO	2.7	22		
CH_3COCH_3	2.8	21		
HCOOH	1.2	47		
CH_3COOH	0.8	6.4		
$\text{CH}_3\text{COOCH}_3$	1.7	7.3		
HCONH_2	3.2	84		
CH_3CONH_2	3.6	60		
		(at melting point)		
HCN	2.6	95		
CH_3CN	3.2	39		
$\text{C}_2\text{H}_5\text{CN}$	3.4	28		

Dipole-moment data from several sources, notably

SIDGWICK, N. V., "Table of Dipole Moments," Gurney & Jackson, London, 1934.

GILMAN, H., editor, "Organic Chemistry," John Wiley & Sons, Inc., New York, 1943.

lie at an angle of 105 deg to one another. On the other hand, the carbon dioxide molecule, also held together by covalent bonds, has no dipole moment. It is nonpolar. Hence, its shape is deduced to be strictly linear.

Another interesting example of the effect of structure on polarity is shown by methane and its chlorinated derivatives. The bonds in methane are all covalent, and the hydrogen atoms are symmetrically disposed about the carbon atoms. The introduction of one chlorine atom to form chloromethane causes a large disturbance in the structural and electrical symmetry. (The chlorine atom is strongly electronegative, *i.e.*, the bonding pair of electrons is closer to the chlorine than to the carbon.) A large dipole moment results. Successive introductions of chlorine tend to restore the symmetry until, when carbon tetrachloride is reached, the molecule is again symmetrical and has no dipole moment (Table 2-3).

From a study of the several series of compounds in Table 2-3, it is evident that the dielectric constant (for liquids) is a better criterion than dipole moment for judging the over-all polarity. It is likewise evident that certain structures such as $-\text{CH}_2-$, $-\text{CH}_3$, and C_6H_6 are practically nonpolar. Others such as $-\text{OH}$, $-\text{CONH}_2$, $-\text{CONH}-$, and $-\text{C}\equiv\text{N}$ are strongly polar, while still others like the $-\text{COO}-$ group lie in between. There are no sharp lines of demarcation. Furthermore, one part of a molecule may be strongly polar, whereas other parts may be mildly polar.

TABLE 2-4. BOILING POINT AND POLARITY IN ORGANIC COMPOUNDS OF SIMILAR MOLECULAR WEIGHTS

Compounds	Boiling point, deg C	Dipole moment, debyes	Dielectric constant (at about 20 C)
$n\text{-C}_4\text{H}_9\text{CH}_3$	36.2	0	1.8
$\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$	34.5	1.1	4.3
$n\text{-C}_4\text{H}_9\text{NH}_2$	76	1.3	5.4
$n\text{-C}_4\text{H}_9\text{Cl}$	78	2.0	9.6
$\text{C}_2\text{H}_5\text{COC}_2\text{H}_5$	102	2.7	17
$n\text{-C}_4\text{H}_9\text{OH}$	118	1.7	18
$n\text{-C}_4\text{H}_9\text{COOH}$	187	...	2.7
$i\text{-C}_4\text{H}_9\text{COOH}$	177	0.7	2.8
$n\text{-C}_4\text{H}_9\text{CONH}_2$	3.7	
$i\text{-C}_4\text{H}_9\text{CONH}_2$	232		

If similar compounds of equal molecular weight are compared, their boiling points are a fair measure of the intermolecular forces of attraction, as discussed later in this chapter. Such a group is presented

in Table 2-4. It will be seen that there is a generally good correlation between polarity and intermolecular attractive forces, with one notable exception. The acids have comparatively high boiling points in spite of low dipole moment and dielectric constant. As will be explained later, double molecules of the acid form, due to hydrogen bonding. The resulting molecules are thus twice as large as expected, and hence the attractive forces between them are greater than expected. This is one of the reasons why polarity is not an absolute measure of molecular behavior.

212. The Orientation Effect. That polar molecules or polar parts of molecules can exert attractive forces on one another is readily understood. The unlike poles of the permanent dipoles attract others of opposite sign either in parallel or in antiparallel arrangement (Fig. 2-3). This is called the *orientation effect*. Thermal agitation always tends to upset these alignments, so that this type of secondary

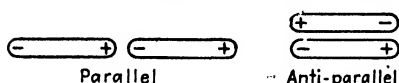


FIG. 2-3. Orientation effect between dipoles.

valence force is highly dependent upon temperature.

213. The Induction Effect. Attention has already been called to the fact that, if an electrical system ordinarily devoid of dipole moment is placed in an electric field which causes a relative displacement of the positive and negative charges, a moment is induced. For many molecules it has been found that an electric field causes slight displacements of the electrons and nuclei, thus leading to such an induced moment. The degree to which this takes place is called the *polarizability* of the molecule; and since the moment is induced, the phenomenon is called the *induction effect*. Since the permanent dipole of one molecule can induce a moment in a second molecule, this effect is particularly important in the attractions occurring between polar and nonpolar compounds. The induction effect is slightly dependent upon temperature.

214. The Dispersion Effect. The discovery of this effect was a by-product of the statistical-mechanical treatment of the covalent bond. It is a matter of fact that molecules completely devoid of dipole moment can nevertheless exert intermolecular attractions upon one another. Thus, in hydrogen or the noble gases the orientation and induction effects are zero. Yet the molecules attract one another. This type of secondary valence force arises from the temporary relative displacements of the nuclei and electrons during the vibration of the several parts of the molecule with respect to one another. These displacements result in temporary dipoles (or quadrupoles) that make intermolecular attractive forces possible. The *dispersion effect* is exhibited by all molecules and is independent of the temperature.

The contributions of the three types of secondary valence forces and

their relative magnitudes in different substances are presented in Table 2-5.

TABLE 2-5. RELATIVE MAGNITUDES OF MOLECULAR-INTERACTION EFFECTS

Molecule	Dipole moment, debyes	Orientation effect at 20 C	Induction effect	Dispersion effect	Normal boiling point, deg C
He	0	0	0	1.23	-268.9
H ₂	0	0	0	11.4	-252.7
N ₂	0	0	0	57.2	-195.8
CH ₄	0	0	0	112	-161.4
CO ₂	0	0	0	152	- 78.5 (subl.)
Cl ₂	0	0	0	321	- 34.6
CO	0.12	0.0034	0.057	67.5	-192.0
HCl	1.03	18.6	5.4	111	- 85.0
HBr	0.78	6.2	4.05	185	- 67.0
HI	0.38	0.35	1.68	370	- 35.5
NH ₃	1.5	84	10	70	- 33.3
H ₂ O	1.84	190	10	47	100.0

Data from several sources, notably

MARGENAU, H., *Rev. Modern Phys.*, **11**, 1 (1939).

215. The Hydrogen Bond or Bridge. A particularly important, and in some respects unique, secondary valence force is the hydrogen bond, or hydrogen bridge. Although introduced into organic chemistry in 1913, general recognition of its importance did not take place until about 1935. Because of its widespread occurrence, Pauling considers that "the significance of the hydrogen bond in physiology is greater than that of any other single structural feature." In spite of the fact that the name *hydrogen bridge* is probably a better, more descriptive one, common use is made of the term *hydrogen bond*.

The hydrogen bond occurs when an atom of hydrogen is attracted by rather strong forces to *two* atoms instead of only one. Since the hydrogen atom has only one stable orbital and can form only one covalent bond, it is now generally recognized that the hydrogen bond is largely ionic in character, with the hydrogen atom oscillating between the other two atoms involved in the bonding. Hydrogen bonding requires electronegative structures and is strong in the presence of strongly electronegative atoms bearing unshared pairs of electrons. The strength of the bonding increases with increase in the electronegativity of the two bonded atoms and decreases with increase in their size. Thus fluorine forms very strong hydrogen bonds, oxygen weaker ones, nitrogen still weaker ones. Chlorine, although strongly electronegative, exhibits rela-

tively little hydrogen-bond-forming power. This may be attributed to its large size, which results in weak electrostatic attractions. Hydrogen bondings involving oxygen and nitrogen atoms are particularly important in the organic field owing to their extensive occurrence. Hydrogen-bond energies range from 5 to 10 kcal per g mole (Table 2-6). The hydrogen

TABLE 2-6. PROPERTIES OF HYDROGEN BONDS

Bond	Bond length, Å	Dissociation energy, kcal/g mole
F . . . H . . . F	2.25-2.51	6.2
O . . . H . . . O	2.30-2.50	5.9-10.2
N . . . H . . . N	2.65	
C . . . H . . . N		6.1-7.8
N . . . H . . . F	2.63	6.0
C . . . H . . . O		4.1-6.0
N . . . H . . . O	2.76-2.88	6.0-6.8

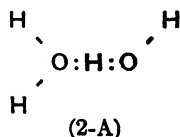
HUGGINS, M. L., *J. Org. Chem.*, **1**, 407 (1936).

bond thus occupies a unique intermediate position and may be considered either as a strong secondary valence or a weak primary valence force. Bond and bridge values in high polymers are summarized in Table 2-7.

TABLE 2-7. BOND AND BRIDGE VALUES ORDINARILY ENCOUNTERED IN HIGH POLYMERS

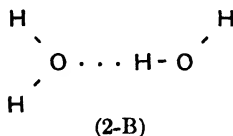
Type of force	Energy value, kcal/g mole	Interatomic or intermolecular distance, Å
Secondary valence bridge.....	0.5-5	3-5
Hydrogen bond, or bridge.....	5-10	2-3
Primary valence.....	50-200	1-2

Water molecules afford a splendid example of hydrogen bonding. An electronic representation of the bonding between two water molecules follows. The hydrogen atom involved is shown in heavier type.



It will be noticed that the hydrogen bond has some of the characteristics of the coordinate bond. A representation frequently used is a dotted

line extending from the hydrogen atom to one of the two atoms involved in the bridging.



This symbol implies a bond not sufficiently strong to be considered primary but nevertheless strong enough to be represented in the molecular structure. The so-called "abnormal" behavior of water, the alcohols, and many other associated liquids is attributable to hydrogen bonding. In water, hydrogen bonding can be particularly extensive since each molecule has two hydrogen atoms available for bonding.

Table 2-8 illustrates the effect of hydrogen bonding on intermolecular forces of attraction and hence on boiling point. The effect that hydrogen bonding can exert on solubilities is nicely illustrated by the liquids listed in Table 2-9.

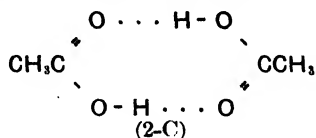
TABLE 2-8. HYDROGEN BONDING AND BOILING POINT

Compound	Hydrogens available for hydrogen bonding	Normal boiling point, deg C
HOH	2	100
CH ₃ OH	1	65
CH ₃ OCH ₃	0	-24

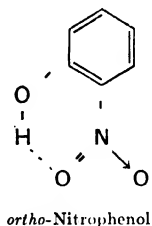
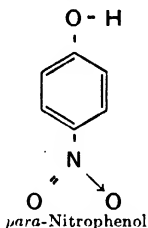
TABLE 2-9. HYDROGEN BONDING AND SOLUBILITY

Substance	Hydrogens available for hydrogen bonding	Solubility in water at 20 C, g/100 g solution
CH ₂ Cl ₂	2	1.96
CHCl ₃	1	0.80
CCl ₄	0	0.08

Chelation is ring closure that arises through coordination in systems containing donor and acceptor centers. There are many instances of chelation via hydrogen bonding. One example is the formation of stable double molecules of organic acids such as acetic.



Another is afforded by *ortho*-nitrophenol. In *para*-nitrophenol the polar, reactive phenol and nitro groups behave independently since they are at opposite ends of the molecule.



However, when the two groups are *ortho* to one another, chelation may take place. To some extent this results in a loss of both phenolic and nitro properties. There is a loss in polarity and ability to hydrogen-bond to other molecules. The effect on several important properties is shown in Table 2-10. Comparison of solubilities in water and benzene indicates the effect of chelation in reducing polarity, while comparison of the sol-

TABLE 2-10. EFFECTS OF CHELATION

Property	<i>o</i> -Nitrophenol	<i>p</i> -Nitrophenol
Normal boiling point, deg C.	214.5	279 d
Solubility, g/100 g solvent:		
In H ₂ O, 20 C.	0.69	11.2
In C ₆ H ₆ , 80 C.	148.3	2.83
In CHCl ₃ , about 15 C.	99.7	2.99
In CCl ₄ , about 15 C.	40.4	0.050

ubility of either compound in chloroform or carbon tetrachloride indicates the effect of hydrogen bonding on solubilities.

Strong hydrogen bonding takes place between —OH groups and between >C=O and H—N< groups. As will be seen in later chapters, this is an important factor in the structure and properties of cellulose, the proteins, and other high polymers.

SURFACE EFFECTS

216. A molecule in the interior of a stable solid or liquid phase is surrounded on all sides by neighbors so that the intermolecular attraction is, on the average, the same in all directions. In the surface, however, the attractive force is unbalanced because there are very few molecules in the gas phase. Therefore, the surface molecules are subject to a net inward attraction.

Two ideas are important. (1) In the surface there is a residual field of force—a state of unbalance or unsaturation. (2) In order to extend the area of the surface, work must be done to bring molecules from the interior into the surface against inwardly directed attractive forces. It follows, therefore, that the surface molecules have greater energy than the interior molecules, and this additional energy content is termed the *surface energy*.

Since the surface molecules are under a net inward attraction, the surface always tends to contract to the smallest possible area. Alternatively, since a system tends always to assume an equilibrium condition of minimum free energy, it follows that it strives toward a condition of minimum surface compatible with the external restraints imposed on it. Thus, a drop of liquid or a gas bubble becomes spherical, the configuration involving minimum surface per given volume.

Because of the tendency to contract, a liquid surface behaves as though it were under tension, the so-called *surface tension*, which acts in the plane of the surface and is equal in all directions along the surface. Surface tension is defined as the force exerted in the plane of the surface per unit length perpendicular to the direction of the force. The free surface energy and the surface tension have identical values. The former is the more fundamental concept, although both are useful.

From the above discussion it is readily understood why the surface of a mass behaves very differently from its interior. It is a high-energy region of particular consequence in such phenomena as adsorption, adhesion, wetting, emulsification, foaming, dispersion (of solids in liquids), penetration (of liquids into solids), flotation, the activity of exchange resins, electrical surface resistivity, heterogeneous catalysis, and certain aspects of corrosion.

When two immiscible liquids are in contact, the molecules of each exert an attraction on those of the other at the interface. This partly overcomes the inward pull of each phase upon the molecules of its own kind present at the interface. Thus, the molecules situated at the interface are under different forces from those in the bulk of the system; the interface has a surface energy known as the *interfacial tension*, which is always less than that of the phase with the higher surface tension. For completely miscible liquids the interfacial tension is zero, and there is no interface.

Interfacial tension, whether liquid-liquid, solid-solid, etc., depends upon many factors. But at this point attention is called to the broadly valid generalization that, for reasons which should now be fairly obvious, it is likely to be higher between phases of dissimilar polarity and structure than between those which are similar in these respects. Lowering the

interfacial tension promotes wetting, spreading, emulsification, foaming, etc.

Since the surface is a region of high free energy, it follows thermodynamically that from a liquid melt or solution any component reducing the surface tension will tend to concentrate in the surface. The general term *surface-active agent* is used to describe materials added to a liquid medium to lower surface or interfacial tension. A liquid hydrocarbon does not disperse in water readily since the interfacial tension is high. If a surface-active agent is added, interfacial tension is reduced. Consequently, it is easier to create a new interface, *i.e.*, to break the hydrocarbon mass into fine droplets by mechanical agitation as in the formation of an emulsion.

But the matter goes further than this. Consider sodium oleate, which is a surface-tension depressant for water. This molecule has a strongly polar head and a long nonpolar tail. The attraction of water for the head is much stronger than that for the tail. It should follow that when the oleate molecules concentrate at the surface they should orient with the polar heads inwardly directed and the nonpolar tails pointed toward the external environment. Hydrocarbon character should be imparted to the surface. There is considerable evidence that such surface orientations do, indeed, often occur. If the sodium oleate is used to form an oil-in-water emulsion, each oil droplet has at its surface an oriented layer of the oleate. The outwardly directed heads are soluble in the water phase, the inwardly directed tails in the oil phase. Hence, the droplets, once formed, tend to stay dispersed, rather than to reunite as would be the case if the oleate were not present. In other words, the soap not only promotes breakup into fine droplets but also stabilizes the dispersion. Both functions are important to an emulsifying agent. In many systems, more than one surface-active agent is added to achieve a high degree of stability. Emulsions are of outstanding importance in high-polymer practice (Secs. 425, 843, and 1336).

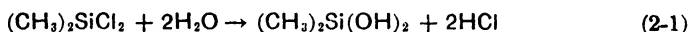
In keeping with the above discussion, the most common structure of commercial surface-active agents is that of a molecule of which the main bulk is nonpolar but which possesses one or more strongly polar points. Such molecules are today "tailor-made" for specific needs such as the promotion of wetting, spreading, emulsification, and detergency. The proportion of molecules in the surface is a very minute fraction of the total molecules in the system. Hence, an efficient surface-active agent need be present in but very small proportions. Wetting agents are usually added in parts per thousand, flotation agents in parts per ten thousand, and antifoaming agents in parts per hundred thousand.

Since a surface is characterized by unbalanced valence forces, it is certain that adsorption or reaction soon occurs at almost any freshly

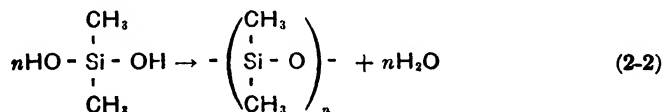
exposed surface. What takes place depends on the specific nature of the valence forces involved, the relative sizes of the surface molecules and of those in the neighboring phase, the concentration of the molecules in the neighboring phase, temperature, etc. Thus, gases are normally adsorbed on glass. They may be driven off by heating to temperatures below the softening point of the glass, the forces being of secondary-valence character. But carbon monoxide is so strongly adsorbed by tungsten that it cannot be driven off. Instead, at sufficiently high temperatures molecules of WCO distil off, showing that in this instance the bonding is of primary-valence magnitude. Both kinds of adsorption may occur even for the identical adsorbent-adsorbate combination. In such cases secondary-valence, or physical, adsorption takes place at low temperatures, and this changes to primary-valence, or chemisorption, on heating.

An *ideally clean surface*, if this be defined as one that is chemically identical with the interior of the phase, is seldom, if ever, dealt with. One must commonly cope with materials adsorbed from the atmosphere (Sec. 1426). In plating processes and the application of surface coatings (Chap. 14) and adhesives (Chap. 15) the condition of the working surface is a vital factor.

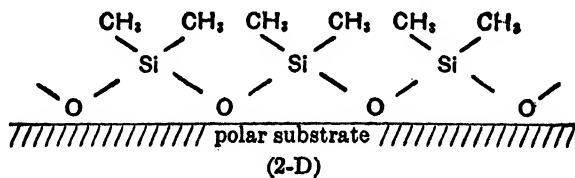
An adsorbed layer that completely covers a surface will obviously convert the original properties of the surface to those of the adsorbate. Glass and paper surfaces have low electrical resistivity owing to the continuous layer of adsorbed water present. On treating such a surface with a mixture of methylchlorosilanes, hydrolysis takes place.



The silicol of Eq. (2-1) is transitory, reacting spontaneously to form a silicone by bifunctional condensation.



Since the glass or paper surface on which this is happening is polar, the resulting silicone chains evidently orient on the surface with the methyl groups outwardly directed as shown in structure (2-D).



The new surface now being hydrocarbon in character, moisture is not adsorbed, and the surface electrical resistivity is very high. Many fabrics and papers may be rendered rainproof or water repellent by this treatment.

FORCES AFFECTING A MOLECULAR SYSTEM

217. A molecular system will be stable or unstable depending upon the forces acting on it and the possible paths by which it can change to a more stable configuration.

Regardless of the particular physical state, acting upon any body of molecules are at least the following influences: (1) molecular forces of attraction; (2) molecular forces of repulsion; (3) thermal agitation; (4) external stress. Of these, the first is a confining, or aggregating, force, the second and third tend to disperse the atoms or molecules, and the fourth may do either, depending upon whether the stress is isotropic or anisotropic. Under favorable conditions, any of them may induce a chemical reaction or physical change.

218. Molecular Forces of Attraction. Evidence for the existence of these forces has been presented and their nature has been discussed in some detail. In any real system more than one of these types of forces are usually acting. There are no sharp lines of demarcation between ionic, covalent, and coordinate bonds, nor do primary bond and secondary bridge energy values constitute separate groups, since intermediate "large" secondary valence forces and "small" primary valence forces cover the gap, so that it is possible to list a continuous "spectrum" of energy values from the almost negligible attraction between two helium atoms to the force between two hydrogen atoms in a hydrogen molecule, the largest bond value per unit mass. For this reason, there is a tendency in modern discussions to drop the distinction between primary and secondary forces and to speak of them all simply as valence forces. At any rate, from the potential energy curve (Fig. 2-1) it is seen that *these forces fall off very rapidly as the interatomic distance increases.*

When the attractive forces are very high, *e.g.*, metals and inorganic salts, the melting and boiling points are high. When the attractive forces are very low, *e.g.*, the noble gases, H_2 , N_2 , O_2 , CH_4 , etc., the melting and boiling points are very low. Most organic compounds, including the monomers used in making high polymers, have an intermediate range of attractive forces and exhibit melting points and boiling points within the limits -100 to $+300$ C.

In many cases it is sufficient to lump together the various forces of attraction, especially in the absence of highly polar structures. For such purposes, the term *internal pressure* is widely used, particularly in

referring to the environment within a liquid. (The term originated as a name for the "pressure" that brings the gas molecules together to form the liquid state.) Various measures are used for the internal pressure, *e.g.*, the attractive-force term in the van der Waals equation. Perhaps the most convenient of these measures is the *cohesive energy density*, a quantity defined as follows:

$$\text{Cohesive energy density} = \frac{\Delta H_b - RT}{V}$$

where ΔH_b is the molar heat of vaporization, RT the perfect-gas value of work of expansion during vaporization, and V the molar volume of liquid.

219. Molecular Forces of Repulsion. That molecular forces of repulsion exist is evident from various behaviors. Only such forces account satisfactorily for the apparently completely elastic behavior of gas molecules upon collision and other phenomena, such as the fact that as increasing pressures are applied to a liquid its compressibility falls off. From the potential-energy curve it is seen that these repulsive forces become prominent when molecules are very close together. They rise very rapidly when attempts are made to crowd them closer than the distance of normal approach.

✓ **220. Thermal Agitation.** Many molecular properties bear out the axioms and deductions of the kinetic theory, which state that a molecule undergoes the several motions of translation, rotation, and vibration, each of which represents part of its total energy content. The energy taken up by a system on being heated goes largely and in many cases entirely to increase these motions.

One of the most important parts of the kinetic theory is the principle of the equipartition of energy. In limited form, this principle states that in a system at a given temperature the kinetic energies of translation of all the particles in the system are identical. This is obviously reasonable; for, during collisions between the particles, transfer of energy will take place until at equilibrium all the particles have the same average kinetic energies, independent of the nature, size, shape, or weight of the molecules as well as their physical states of aggregation. Since the kinetic energy is one-half the product of the mass and the square of the velocity, it follows that molecules of large mass move sluggishly compared with small ones at the same temperature. On this basis, high polymers with the not exceptionally large molecular weight of 40,000 are moving only one-twentieth as fast as "ordinary" molecules with a molecular weight of 100 and less than one-hundredth as fast as hydrogen molecules. As expected, diffusion processes involving high polymers are slow. The actual kinetic energy of translation can be readily calculated by the kinetic

theory. It is a function only of temperature and equals $\frac{3}{2}RT$ for each mole.

The energy of vibration of a system is the important determinant of its stability. When the energy of vibration between two atoms or groups attains and exceeds the potential energy of attraction, dissociation takes place. Similarly, when the energy of vibration between two molecules in a solid attains the potential energy of attraction, the crystal structure dissociates, *i.e.*, melting takes place.

The energy of rotation of a molecule often is a determinant of the state of aggregation of a system. When the molecules of a solid attain sufficient energy to begin to rotate, a change of state takes place (Secs. 513 and 514).

The kinetic energy of translation may be resolved into three degrees of freedom corresponding to three axes in space. Similarly, the kinetic energies of rotation and vibration of a molecule may be resolved into degrees of freedom, their number depending upon the number and arrangement of the atoms within the molecule. In more general form, the principle of equipartition of energy states that the average kinetic energy is the same in each degree of freedom of the particles in a system. This kinetic energy equals $\frac{1}{2}RT$ per mole for each degree of freedom. This more general form of the principle of the equipartition of energy is palpably true, provided that it can be assumed that the energy is "mobile" among the degrees of freedom, *i.e.*, that it is redistributed during collisions. The latter means that during collisions translational energy may be converted into rotational or vibrational, or vice versa. (It so happens that this condition is true only at relatively high temperatures and that there are restrictions on the interchange of energy at ordinary temperatures. The exact calculation of the energy taken up by the rotational and vibrational degrees of freedom is done by means of the quantum theory. These limitations do not affect certain qualitative deductions of the equipartition theory used in this book.)

221. External Stress. Pressure applied to a system is resisted by the molecular forces of repulsion. In many cases, with sufficiently great pressure these forces of repulsion are overcome to the extent that a new configuration of the atoms ensues, *e.g.*, pressure-induced chemical reactions and the several different crystal forms of ice.

An external stress applied nonuniformly such as axial tension or shear may exert important effects including crystallization (Sec. 231) and flow (Chap. 7).

✓ FACTORS DETERMINING THE MAGNITUDE OF INTERMOLECULAR FORCES OF ATTRACTION

222. Effect of Molecular Weight. The normal paraffins above ethane are representable by the formula $\text{CH}_3-(\text{CH}_2)_x-\text{CH}_3$. To all intents

and purposes they may be considered as $-(\text{CH}_2)_x-$, especially when the value of x is appreciable. The molecular densities of these compounds are practically identical, so that, if we consider two members of the series, one in which x is small and another in which x is large, the higher molecular weight member may be assumed to possess a larger volume and hence a larger surface. If it is assumed that the intensities of the residual fields of force around the two molecules are equal, the larger molecule will exert the larger total attractive force on the surrounding molecules. If the two molecules are now considered in the liquid state, the following picture results: Their tendency to leave the liquid, *i.e.*, to volatilize, is due to their translational energy. This tendency will be the same for both, provided only that they are at the same temperature. However, in order to leave the liquid and enter the vapor, they must overcome intermolecular attractive forces. Consequently, the escaping tendency of the larger molecule will be less, resulting in a lower vapor pressure. That is, at constant temperature its vapor pressure should be less, or at constant pressure its boiling point should be higher. This is indeed the case. Normal pentane boils at 36 C, cetane, $n\text{-C}_{16}\text{H}_{34}$, at 288 C. Heptacontane, $\text{C}_{70}\text{H}_{142}$, with a molecular weight of 982, does not boil at all. Before a boiling temperature can be reached, it decomposes. As previously stated, the bonding energies involved in the primary valences holding the atoms of a molecule together are of the order of 20 to 200 kcal per g mole, while secondary forces are much weaker, ranging from 0.5 to 5.0 kcal. But when molecules are large enough and have a large enough surface, the secondary forces bridging them to one another may pile up to the point where, in the aggregate, they are greater than the primary valence force holding two atoms in the molecule together. When this is the case, primary valence bonds will be ruptured before the molecules can be separated against the extensive bridging forces, *i.e.*, thermal decomposition results before a boiling point is reached.

It follows from what has just been said that, as a homologous series is ascended, the boiling point, melting point, tensile strength, and, in fact, any property that might logically be ascribed to intermolecular forces of attraction should increase. This is indeed the case. For example, the heats of fusion of the normal paraffins increase by a regular increment q for each addition of a methylene group. If x represents the number of links in the chain,

$$H_f = xq \quad (2-3)$$

For the normal paraffins, q is 0.610 kcal.

In terms of intermolecular forces, as the molecules become longer, more energy is required to overcome the cohesive forces holding them in the solid state and cause fusion. Furthermore, it has been found that

in a homologous series the melting points increase with molecular weight in accordance with the empirical equation

$$\frac{1}{T_f} = a + \frac{b}{x} \quad (2-4)$$

where T_f is the melting point in degrees Kelvin and a and b are constants. For the normal paraffin series, a is 2.395×10^{-3} , b is 17.1×10^{-3} , and x is again the number of linkages in the chain. For the paraffins containing 12 to 60 carbon atoms, calculated values agree remarkably with

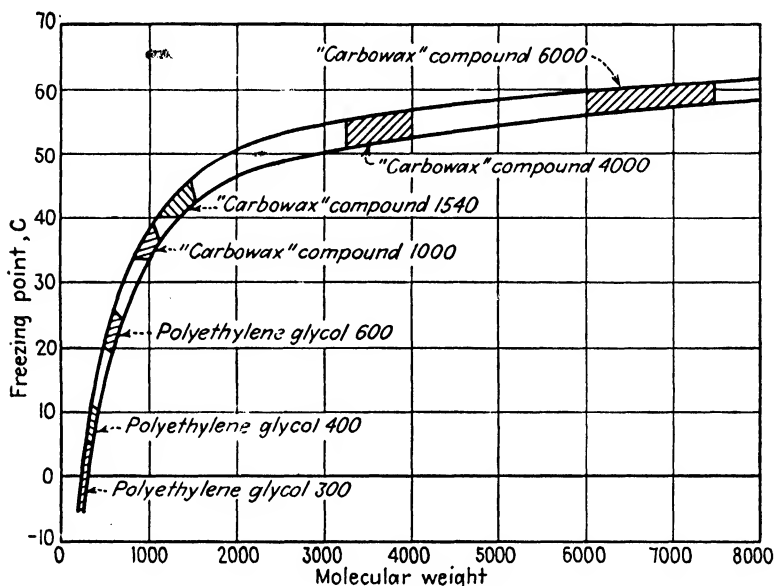


FIG. 2-4. Melting point as a function of molecular weight for a homologous series. The curves mark the freezing ranges and molecular-weight ranges of commercial products. [C. P. McClelland and R. L. Bateman, *Chem. Eng. News*, **23**, 247 (1945). Courtesy of Carbide & Carbon Chemicals Corp.]

the observed melting points. Equation (2-4) has the graphical form shown in Fig. 2-4.

The molecules of any particular species of high polymer at various degrees of polymerization are members of a homologous series just as are the paraffins. In homologous series in general, the plot of melting point vs. molecular weight has the form shown in Fig. 2-4. The importance of the form of the curve can scarcely be overstressed. Time and again when the degree of polymerization is plotted vs. a property that may be reasonably attributed to intermolecular cohesive forces, the curve takes this shape (see Figs. 2-5 and 2-6). The fact that the curve plateaus off should be noted. [In Eq. (2-4), when x attains a high value, b/x becomes

negligible.] When molecular weights reach the polymer range of 10,000 or more, an increase of as much as several thousands often results in little or no observable change in the property in question. A molecular interpretation of this effect is that, after a molecule has reached a certain size,

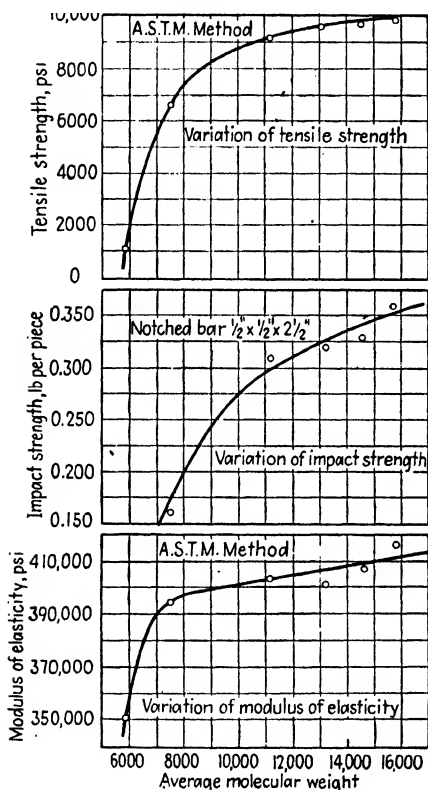


FIG. 2-5. Effect of degree of polymerization on some mechanical properties of a vinyl chloride-acetate copolymer. [G. O. Curme and S. D. Douglas, *Ind. Eng. Chem.*, **28**, 1123 (1936).]

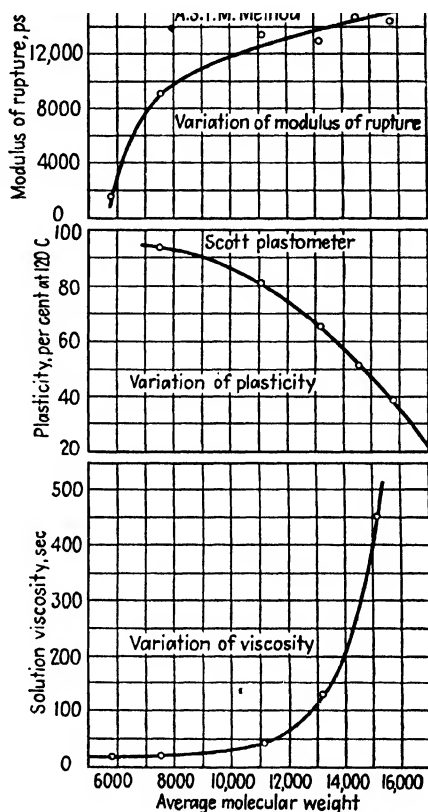


FIG. 2-6. Effect of degree of polymerization on some properties of a vinyl chloride-acetate copolymer. [G. O. Curme, and S. D. Douglas, *Ind. Eng. Chem.*, **28**, 1123 (1936).]

one part is no longer influenced by other parts considerably removed from it.

Among the important properties that vary with the degree of polymerization are softening point, viscosity in solution, tensile and compressive strengths, elastic moduli, solubility, and impact strength. Among those which are essentially independent of or change very little with the D.P. are refractive index, hardness, electrical properties, color, and density.

TABLE 2-11. MOLAR COHESIONS OF VARIOUS LINEAR HIGH POLYMERS

Polymer	Structure	Molar cohesion per 5 Å chain length (assuming coordination number of 4) kcal/g mole
Ethylene	$-(CH_2)_n-$	1.0
Isobutylene	$\begin{array}{c} CH_3 \\ \\ -(C-CH_2)_n- \\ \\ CH_3 \end{array}$	1.2
Butadiene	$-(CH_2-CH=CH-CH_2)_n-$	1.1
Natural rubber	$\begin{array}{c} CH_3 \\ \\ -(CH_2-C=CH-CH_2)_n- \\ \end{array}$	1.3
Styrene	$\begin{array}{c} C_6H_5 \\ \\ -(CH-CH_2)_n- \end{array}$	4.0
Chloroprene	$-(CH_2-CCl=CH-CH_2)_n-$	1.6
Vinyl chloride	$-(CHCl-CH_2)_n-$	2.6
Vinyl acetate	$\begin{array}{c} OCOCH_3 \\ \\ -(CH-CH_2)_n- \end{array}$	3.2
Vinyl alcohol	$\begin{array}{c} OH \\ \\ -(CH-CH_2)_n- \end{array}$	4.2
Cellulose	$\left[\begin{array}{c} \text{CHOH}-\text{CHOH} \\ \diagup \quad \diagdown \\ \text{CH} \quad \text{CH}-\text{O} \\ \diagdown \quad \diagup \\ \text{CH}_2\text{OH} \end{array} \right]_n-$	6.2
Cellulose acetate	Cellulose with acetate groups replacing alcohol groups	4.8
Synthetic polyamides	$-[OC(CH_2)_xCONH(CH_2)_yNH]_n-$	5.8
Silk fibroin	$-(CHR-CONH)_n-$	9.8

223. Effect of Polarity. In the discussion of secondary valence forces, the importance of polarity was brought out. A molecule containing strongly polar structures will exert strong attractive forces on molecules around it. In the absence of such structures the intermolecular forces will be weak. Consider the two linear polymers, polyethylene, $-(CH_2)_n-$, and the polyamide, $-[(CH_2)_5CONH]_n-$. The methylene link is practically nonpolar, whereas the amide linkage is strongly polar. Assuming D.P.'s such that the chains are of equal length, the forces of attraction between the polyamide chains will be considerably stronger than those between the polyethylene chains. This is reflected in higher tensile strength, melting point, and crystallizing tendencies in the polyamide. Extensive hydrogen bridging can take place between the polyamide chains [structure (5-F), page 213].

Table 2-11 contains valuable data on various linear high polymers. The second column shows the structure of the mer; the last column lists the energy values of the secondary forces for a length of 5.0 Å along the chain, assuming that each chain is surrounded by four others (coordination number of 4).

224. Effects of Symmetry and Orientation. It will be recalled that intermolecular forces of attraction fall off very rapidly as the intermolecular distance increases. Consider a mass of linear polymers. If the residual fields around the molecules are to exert a maximum effect, it is essential that the molecules be packed as closely as possible. Obviously, the best possible arrangement from this standpoint is perfect parallel alignment or orientation. It has been experimentally established that the molecules of a linear-polymeric mass can be aligned and that the forces of attraction increase with the degree of alignment. When the individual chains are streamlined, *i.e.*, when there are no branches, side chains, or "bumps," the orientation process is easier to effect. On the other hand, chain bulkiness or irregular architecture renders orientation and close packing difficult. That is, molecular streamlining, or *architectural symmetry*, fosters close packing and large total intermolecular attractive forces.

Consider now a mass of chain molecules containing strong centers of attraction such as strong permanent dipoles *at regular intervals* along the chains. Alignment could conceivably bring all the attractive centers into juxtaposition as in Fig. 2-7a. In this figure, the dots indicate dipoles, and each is exerting a strong orientation effect upon its neighbors. The intermolecular forces between the chains are thus acting at a maximum. On the other hand, with *irregular spacing* of the same attractive centers along the same chains, even perfect alignment leaves some of the attractive centers "unpaired" as in Fig. 2-7b. These unpaired centers con-

tribute to the interchain attractive forces by exerting an induction effect on neighboring chains; but this effect is relatively weak, and the total attractive forces obviously cannot be so great as in Fig. 2-7a. Thus, the *recurrence symmetry*, i.e., the regularity with which similar structures recur along polymeric chains, is also a factor in determining the total force of attraction between chains, especially when they are oriented.

Henceforth the unqualified term *molecular symmetry* will be used to

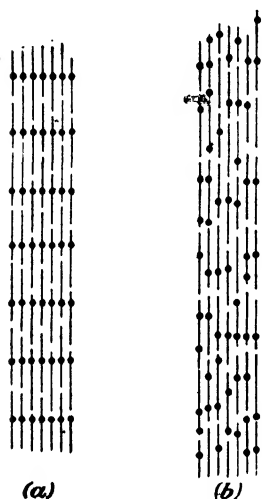


FIG. 2-7. Schematic representation of oriented linear polymers. Dots indicate strong attractive centers.

cover both architectural and recurrence symmetry. A knowledge of the structure of high-polymer chains enables one to predict qualitatively how nearly perfect orientation can be and how readily it may take place.

225. Summary. The total forces of attraction acting between chain molecules depend upon at least four factors:

1. The average chain length, i.e., average molecular weight or degree of polymerization
2. The polarity of the structures on the chains
3. The architectural and recurrence symmetry
4. The degree of alignment or orientation

The intermolecular attractive forces are always being opposed by thermal agitation. The effect of chain length is mainly extensive, i.e., the total force of attraction increases owing to greater molecular surface while the force per unit area remains constant. By contrast, polarity is intensive; the more strongly polar the structure, the greater the attractive force per unit area. Finally, it is important to bear in mind that the effects of these factors are relatively short range so that minor and subtle changes in structure may notably affect the physical behavior of high polymers.

FACTORS CONTROLLING EQUILIBRIUM AND RATE

226. Systems differ greatly in their response to changes in conditions. The response is governed by (1) equilibrium factors and (2) rate factors. Corresponding to these are the two broad divisions of physical science, thermodynamics and kinetics. Applications of their principles to high-polymer systems are numerous and of fundamental consequence as in all physics, chemistry, and engineering.

227. Equilibrium Factors. Under a given set of conditions, a system tends to assume a stable, or equilibrium, state. With any change in the

conditions, the system tends to change spontaneously to a new equilibrium state. Thus, change in temperature, mechanical stress, or electric field results in a shift of the equilibrium point, and a major problem of thermodynamics is the quantitative calculation of these effects of external conditions on this point. Toward this end, three thermodynamic quantities, enthalpy, entropy, and free energy, are outstandingly useful.

The enthalpy change accompanying any constant pressure process is the heat interchanged with the surroundings. When the system absorbs heat, its enthalpy increases and the sign of the change is positive. Typical for a physical process is the heat of fusion absorbed during melting [Eq. (2-3)]. The heat evolved during a chemical reaction at constant pressure represents the decrease in the enthalpy of the system that accompanies the molecular changes involved in the process.

The entropy of a system is a measure of its state of organization. If a system changes to a more disorganized state, its entropy increases. Thus, during the fusion of a crystalline solid there is an increase in entropy. The tendency of systems to degenerate to more disorganized conditions of higher entropy is a major thermodynamic behavior. If a system is so simple that all its various configurations are calculable, its entropy change may be calculated from the change in probability of these configurations. In most systems, however, such calculation is not possible, and entropy change must be determined from experimental data.

The quantitative measure of the ultimate stability of a system is its free energy. If a system under a set of constant external conditions can exist in a state of lower free energy, it tends to change to that lower state spontaneously. When no further change can take place, the system is in equilibrium; in other words, equilibrium may be described as the state of minimum free energy.

The enthalpy, entropy, and free-energy changes in any system under a constant set of external conditions (temperature, mechanical stress, electric field, etc.) are related by the equation:

$$\Delta G = \Delta H - T\Delta S \quad (2-5)$$

where G is the free energy, H the enthalpy, T the absolute temperature, and S the entropy.

Consider the process of fusion of a crystalline solid:

$$\Delta H = H_d - H_c \quad \text{and} \quad \Delta S = S_d - S_c$$

where H_c , H_d , S_c , and S_d are enthalpies and entropies in the crystalline (ordered) and liquid (disordered) states, respectively. In the case of ice below 0°C, if melting did occur, the enthalpy increase ΔH would be larger than the increase in the entropy term $T\Delta S$; as a consequence, the ice

does not actually melt. At 0 C, these two terms are equal so that ice and water can remain in equilibrium ($\Delta G = 0$). Above 0 C, the enthalpy increase is less than the increase in the entropy term and the ice melts spontaneously.

228. Rate Factors. While the thermodynamic relations just described constitute powerful tools for determining the ultimate effect of various conditions upon the equilibrium point, they provide no answer to the vital question of how fast equilibrium will be reached. Thus, the rate of a process is not usually determined by the free-energy decrease occurring. A gaseous mixture of hydrogen and oxygen is apparently stable and may be kept at room temperature indefinitely without measurable change despite the fact that conversion to water is accompanied by a large decrease in free energy. We must turn to kinetics for the answer.

Physical and chemical processes fall into two more or less distinct groups. In the first group are those processes whose rates change very greatly with temperature—temperature dependence is exponential. The rate of flow (laminar) of a liquid through a capillary is a physical example of this kind. A chemical example is the rate of most organic reactions, such as esterification. In all these processes, the controlling factor is what is known as *activation*; i.e., a molecule or other particle involved in the process cannot undergo the process until it has acquired, by thermal fluctuations, an amount of energy considerably in excess of the average thermal energy of its fellows.

In the second group are those processes whose rates are not highly temperature dependent but, rather, are controlled most strongly by conditions other than activation. The flow of gas through a capillary is a physical example. In sharp contrast to the flow of liquids, which was cited as a typical example of the first group, temperature exerts a much less important effect on this process, which is controlled more by molecular collision. For example, on increasing the temperature from 0 to 100 C, the fluidity (reciprocal of viscosity) of water vapor *decreases* 31 per cent, whereas that of liquid water *increases* 532 per cent. Ionic reactions are chemical examples of this group of processes. They proceed at such a rapid rate that they come to equilibrium practically instantaneously, regardless of temperature. Stated in other words, ions are already so thoroughly active that further activation is of little consequence. Hence, when an acid solution is being neutralized by an alkali, the rate for the process is determined entirely by the rate of mixing. The distinguishing characteristic of this group of processes, however, is not necessarily rapid rate but rather a rate that does not vary markedly with temperature.

One and the same process may fall into either behavior group depending upon conditions. For example, in a slowly alternating field, the

response of a dipole is such that it is always oriented in and in phase with the field; but if the frequency of the field is increased, eventually a point is reached where the dipole begins to lag behind the field and the rate of orientation becomes dependent upon an activation process (Secs. 1005 and 1006). Similarly, there are chemical reactions whose rates are low enough, at, say, room temperature to be measurable. In the neighborhood of room temperature, the reaction rate depends on activation and is highly temperature dependent. These same reactions go faster with increase in temperature and may eventually become "instantaneous," in which case dependence on temperature becomes secondary and rate is controlled by other factors such as thermal conductivity.

229. Activation Energy. The activation process is illustrated in Fig. 2-8. Particles in the initial state i require the absorption of a definite amount of energy U to reach the activated state x , from which they can then proceed to the final state f . On a potential-energy diagram, the initial and final states are valleys, and the activated state is the mountain separating them. The *activation energy* is that required to lift particles over the mountain and is the chief

factor in determining the rate of the process. In simple cases of chemical catalysis, the catalyst increases the rate by decreasing the energy required for activation, *i.e.*, by providing a mountain pass or tunnel at a lower level.

The Arrhenius equation relates the rate of a process requiring activation with temperature.

$$r = Ae^{-U/RT} \quad (2-6a)$$

or

$$\ln r = -\frac{U}{RT} + \text{constant} \quad (2-6b)$$

where r is the reaction-rate constant, U the molar activation energy, R the molar gas constant, and A a constant. This equation, originally empirical, now rests on sound theoretical bases. According to theory, in chemical reactions the constant A is proportional to the number of collisions of reacting molecules; accordingly, it is variously termed the *collision number* or the *frequency factor*.

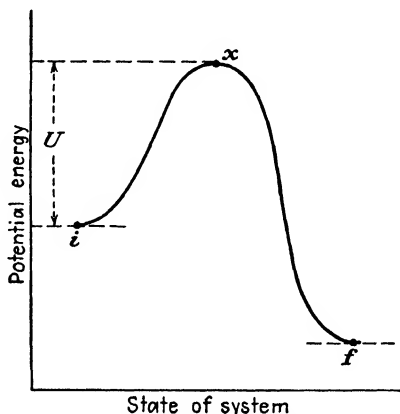


FIG. 2-8. Change of potential energy in a process.

The Arrhenius equation may be said to be perfectly general, applying to nuclear reactions, chemical reactions, and physical changes. In nuclear reactions the activation energy is so astronomically high that the probability of a system receiving such energy is normally vanishingly small. However, in the interiors of stars the temperatures reach millions of degrees so that nuclear reactions proceed with appreciable speed.

The activation energies of chemical reactions vary considerably. For ordinary measurable reactions they range from 16 to 60 kcal per g mole. There are undoubtedly higher and lower values, but experimental difficulties prevent their measurement. With low values of the activation energy, the reactions go very rapidly. With high values of the activation energy, the reactions go too slowly under ordinary conditions, and accurate experimentation at high temperatures is difficult. The highest activation energies are probably for the dissociation of simple gaseous molecules, since these take place only at high temperatures (1000 to 3000 K). The activation energy for dissociation must at least equal the dissociation energy of the weakest bond in the compound (Table 2-1).

"Instantaneous" reactions such as those between ions presumably have such low values that, as previously stated, activation is not the controlling factor in the rate. Reactions involving polar compounds have low activation energies so that they proceed relatively rapidly. The converse is true for reactions involving nonpolar compounds.

At first thought, physical processes such as the flow of a liquid seem quite different from chemical reactions. However, from a molecular point of view they are similar. Thus, in chemical reactions the atoms in one equilibrium position, *i.e.*, a chemical compound, surmount an energy barrier and get into a new equilibrium position, *i.e.*, a new chemical compound; and, in the flow of a liquid under a stress gradient, the molecules in one equilibrium position similarly surmount an energy barrier and get into new positions, causing the liquid to flow. The change in rate of flow with temperature is given by the Arrhenius equation. As temperature falls, the liquid flows more slowly because fewer molecules have sufficient energy to surmount the energy barrier and move to more stable positions.

Activation energies have been measured for a variety of physical processes, *e.g.*, viscous flow, mechanical creep, and dielectric relaxation. The known activation energies for these physical processes vary more widely than those for chemical reactions, owing to the availability of observational techniques for both very rapid and very slow processes. The range is represented by 1.5 kcal for the viscous flow of *n*-pentane and 97 kcal for the creep of hard rubber. Very high values indicate the presence of a large number of restraints that must be overcome before displacement of the units takes place.

230. Relaxation. For physical processes several concepts are used in parallel and frequently interchangeable form. These are viscosity, fluidity, relaxation rate, and relaxation time. Since these quantities are defined in different terms for different applications, their exact definition will be left till later.

It may first be helpful to review analogous terms used for chemical and nuclear processes. The reaction rate is usually expressed as the amount of material converted per unit time. However, alternatively the reaction time may be used; this is the time required for a particular fractional conversion, *e.g.*, the half life of a radioactive element. The reaction time therefore varies inversely as the reaction rate.

Relaxation is the time lag in the response of a system to a change in the physical forces to which it is subjected. The relaxation rate of a physical process corresponds to the reaction rate of a chemical process. For tensile creep, for example, it may be expressed as the fractional increase in length per unit time. The concept of relaxation rate is particularly useful for cyclic stress, and in such case it is expressed as a frequency in cycles per unit time. The relaxation time varies inversely as the relaxation rate, just as reaction time varies inversely as the reaction rate.

The viscosity is used quantitatively to express the resistance of a fluid to flow (Secs. 702 *ff.*). Fluidity is the reciprocal of viscosity and measures the ease with which a fluid flows. These same terms are employed in describing other physical processes, even though no mass flow takes place. Thus, in dielectric relaxation it is useful to postulate that the viscosity of the material resists the rotation of dipoles in a changing field. In such usage the viscosity is taken to be proportional to the relaxation time.

For physical processes the activation energy is often expressed in molecular terms:

$$r = Ae^{-U/RT} = Ae^{-u/kT} \quad (2-6c)$$

where r is a reaction rate or a relaxation rate or a fluidity, u the molecular activation energy, and k the Boltzmann constant. The reciprocal form of the Arrhenius equation is often used.

$$\lambda = Be^{U/RT} = Be^{u/kT} \quad (2-7a)$$

or

$$\ln \lambda = \frac{U}{RT} + \text{constant} \quad (2-7b)$$

where λ is a relaxation time or a viscosity and B is a constant, the reciprocal of A . Activated processes are characterized by a linear relationship

between a rate or time factor plotted logarithmically vs. temperature (Fig. 10-19) or more properly reciprocal temperature (Figs. 10-10 and 13-15).

CRYSTALLINITY

231. If by *crystallinity* is meant an ordered arrangement and regular recurrence of atomic or molecular structures in space detectable by x-ray diffraction analysis, then, among high polymers, materials are encountered running the entire gamut from the highly crystalline to the almost completely amorphous.

Obviously, in a linear-polymeric mass, a basic requirement for crystallinity is parallel alignment among the chains. But this in itself is not enough since it is also obvious that, if the recurrence symmetry is poor, a high order of crystallinity is impossible even with perfect chain alignment.

Because of their very length one might expect linear high polymers to be relatively difficult to arrange in an orderly fashion. Yet such order is attainable. Certain regions in any natural fiber such as silk, cotton, or flax exhibit a high degree of geometric organization where the chain molecules are perfectly aligned. These regions are called *crystallites* or *micelles* and diffract x rays in such a manner that a definite pattern is produced on a photographic plate (Secs. 502 *ff.*). They exhibit distinct anisotropy (Fig. 2-11a). In high polymers these crystallites are not all of the same size and do not possess well-defined faces or edges. In many ways they are comparable with the grains of a polycrystalline metal. The amount of crystallite material and the degree of perfection of alignment of the molecules may be ascertained from the intensity and sharpness of the rings of the x-ray powder diagram (Fig. 5-7a).

Even in a sample that possesses well-defined crystallites there are always regions in which chain alignment is poor. These are called *amorphous* or *intermicellar* regions. They do not diffract x rays regularly and cause a background diffusion to appear on the photograph (see Figs. 5-38 and 5-39). The intensity of this background diffusion is a measure of the relative amount of noncrystalline material in the sample.

There is considerable evidence from x-ray studies and other sources that the individual chain molecules of a fibrous high-polymer mass pass continuously through successive crystalline and amorphous regions as shown in Fig. 2-9. On this basis, the mass consists of crystallites joined to one another by "molecular ropes." This concept is of great theoretical importance. If one chain ends and another begins *inside* a crystallite, discontinuity of structure is virtually eliminated (points *A* and *B* of Fig. 2-9). On the other hand, if chain termini occur in an amorphous region, definite discontinuity results. One of the molecular ropes joining the

crystallites is "broken," and the resistance of the mass to tension is considerably lowered.

If the molecular mass shown in Fig. 2-9 were subjected to tension, one might expect a greater degree of parallelism among the crystallites and chain molecules to result. This is borne out by experiment (Fig. 2-11b). When a fiber is subjected to tension, the result is a sharpening and increase in intensity of its x-ray pattern and a simultaneous falling off in the amount of background diffusion (Fig. 5-35). These changes are accompanied by an increase in density.

Not only may tension cause orientation of previously existing crystallites, but it may also induce crystallization of amorphous material. Let us theorize about a single chain molecule isolated in space. It would not remain straight or extended. Rotation would take place around single bonds. Thermal agitation would cause a whipping about and wriggling. Its "shape" would be that of a statistical coil or tangle representing a configuration of high thermodynamic probability (high entropy). If the molecule were devoid of strong attractive centers, it would assume all possible coiled positions with equal readiness. If, on the other hand, there were strong attractive centers along the chain, the fields around these points might hold the molecule in a certain preferred coil or fold of considerable relative stability. This would represent a sort of *intramolecular* or *internal crystallinity*. In either event, if tension could be applied to the ends of this long, coiled molecule, a great increase in length would result from pulling it to its fully extended position. Upon release of the tension it would retract more or less rapidly to the short, coiled shape. We have here the clue to rubbery "stretch." The lower the internal viscosity, *i.e.*, the shorter the relaxation time, the more rapid the retraction.

The amount of reversible extensibility that the molecule can exhibit depends upon several structural factors. First there is the matter of length. A short molecule like that of water can undergo very little change in dimension during alternate application and release of tension. Obviously it cannot coil and uncoil; furthermore, normal bond lengths

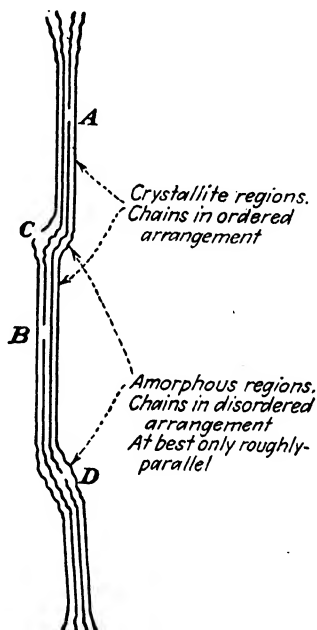


FIG. 2-9. Schematic representation of chain molecules passing through successive crystallite and amorphous regions.

and angles cannot be changed very much. (Ice, metals, and salts show reversible elongations of only about 0.1 per cent.) But in a long polymeric chain the dimensional change could be enormous. (In natural rubber, the kinetically controlled reversible extensibility under discussion may be 1,000 per cent or more.) A second factor is the inherent flexibility of the molecule. A long paraffin hydrocarbon chain would be very

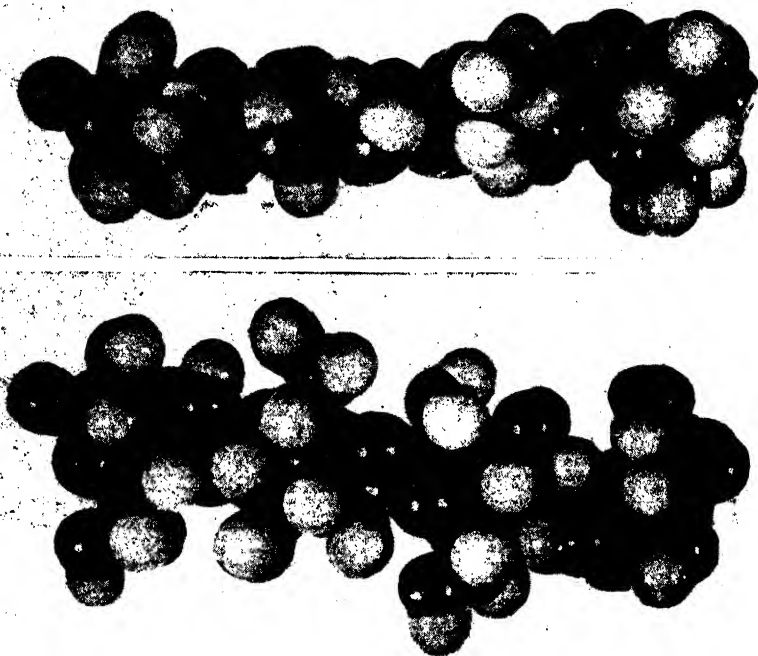


FIG. 2-10. Scale model of a portion of a cellulose molecule. (*E. Ott in "Chemistry of Large Molecules," Burk and Grummüt, editors, Interscience Publishers, Inc., New York, 1943.*)

flexible since free rotation could occur around all its bonds. By contrast, a cellulose molecule would lack flexibility. It consists of rigid 6-membered rings joined through oxygen bridges (Table 1-1). A molecular scale model¹ of a cellulose chain reveals that steric hindrance prevents free rotation at the oxygen bridges (Fig. 2-10). The molecule therefore lacks flexibility and is inherently incapable of undergoing as much folding or coiling as a paraffinic chain.

If, now, we start with a mass of many coiled and entangled chains and the consistency is such that it can be drawn out, then, upon the

¹ Hirschfelder models, especially those in which the "atoms" are joined with snap fasteners, are of great value in representing molecular structure and behavior.

application of tension it should be possible for individual chains not only to disentangle and straighten but also to slip past one another. If, during this postulated drawing process, chain straightening actually occurred, mutual attraction between the chains would increase owing to the closer packing that would accompany the molecular alignment. This increase in the forces of attraction between the chains not only would help to induce their further parallelization but also would tend to keep them parallel once they had become so. This would be particularly true if the chains were symmetrical and strongly polar. The ultimate of this

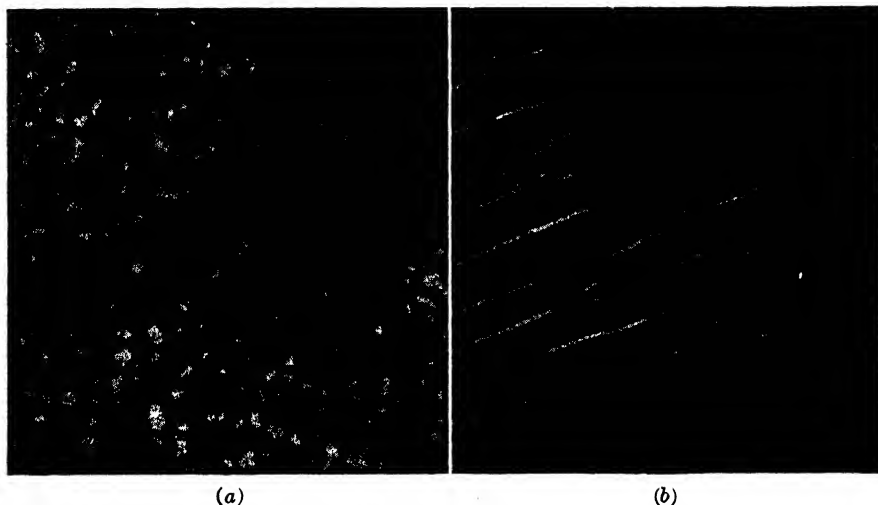


FIG. 2-11. Photomicrographs ($\times 1,000$) by polarized light of polyethylene. [F. C. Hahn, M. L. Macht, and D. A. Fletcher, *Ind. Eng. Chem.*, **37**, 526 (1945).]

process is the formation of a perfectly oriented, perfectly crystalline mass. (This extreme state is never actually attained; for crystallization starts at different points in the mass, and mutual interference by growing crystallites always results in a certain portion remaining in a disordered condition.)

That crystallization and orientation do actually accompany the drawing of many linear polymer masses is indicated by the following changes, most or all of which accompany the process:

1. Whereas, before drawing, the tensile strength of the mass is uniform along all axes, after drawing it is unbalanced, being much higher along the axis of drawing than in any other direction.
2. The drawn mass exhibits anisotropy in many other mechanical and physicochemical properties, for example, birefringence and anisotropic swelling in solvents.

3. The x-ray pattern grows sharper and the intensity of the background diffusion decreases (see Figs. 5-18, 5-35, and 5-39).
4. The solubility of the mass decreases.
5. The softening point increases.
6. The density increases.
7. The luster increases.

The drawing operation, of outstanding practical importance, is illustrated in Fig. 2-12. In the manufacture of man-made fibers such as rayons, nylons, polyvinylidene chloride, and polyvinyl chloride-acetate, one step of the process is a drastic stretching of the filaments. This improves their tensile strengths severalfold. As a matter of fact, it is not

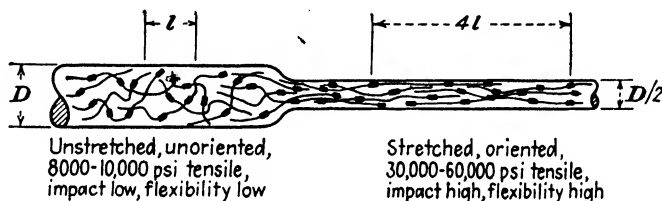


FIG. 2-12. Comparison of unoriented and oriented saran (polyvinylidene-vinyl chloride). [W. C. Goggin and R. D. Lowry. *Ind. Eng. Chem.*, **34**, 327 (1942).]

until after they have been drawn that they possess the tensile strength required of commercial textile fibers. Crystallinity may also be induced by unidirectional rolling of sheets or by slow, controlled evaporation of a proper solvent from a high-polymer solution.

STRESS-INDUCED ORIENTATION

232. In the previous section evidence was presented to show that orientation could be induced by the application of external stress. Whether the chains or crystallites *remain* in the straightened, mutually aligned condition when the external tension is released or whether they return to a coiled or folded position depends on which of the two arrangements represents that of minimum free energy.

Thermal agitation always tends to disarrange the chains, whereas the intermolecular forces of attraction tend to hold them in their oriented positions. At one extreme, if the chains are very flexible, the intermolecular forces of attraction inherently low, and the symmetry such that fitting of the chains into a regular lattice is difficult, the material will tend to retract upon release of the external tension. It will possess a high order of *reversible extensibility*¹ and be flexible and soft. This is the

¹ The term *reversible extensibility* as used in this text will mean the amount of elongation a material can undergo without suffering a permanent set. The authors consider it a better term than *elasticity* for describing the property of high polymers.

state of affairs typical for a rubber or *elastomer*. The hydrocarbon, natural rubber, is an excellent example. At the other extreme, if the chains are inherently rigid, the intermolecular forces intense, and the symmetry such that the molecules fit readily into a lattice, then crystallinity, once induced, will tend to be permanent. Such a material would be a typical fiber. Compared with a rubber, it would incline toward rigidity, hardness, and lack of *reversible* extensibility. With regard to this latter point, once the chains of a linear high-polymer mass have been fully extended in an oriented lattice, any further extension can take place in one of two ways. Either molecular slippage takes place, in which case the extension is not reversible and a permanent deformation results, or elongation takes place through distortion of the normal bond angles. This latter extensibility is reversible but must of necessity be small since any large distortion of the bond angles results in molecular rupture. Good examples of fibers are silk, linen, and nylon.

In intermediate cases, the material will be neither a rubber nor a fiber. Its behavior will depend very greatly on temperature and external stresses. Such a material is what is ordinarily called a *plastic*. Generally speaking, a plastic should possess sufficient rigidity, dimensional stability, and mechanical strength (preferably isotropic) at room temperature to serve as a useful household article, gadget, or stressed structural part and yet be of such character that it may be molded to shape by the application of reasonable temperatures and pressures. In theoretical terms, the intermolecular forces of attraction should be neither too high nor too low.

There are thus no intrinsic differences among rubbers, plastics, and fibers. Rather the difference is a matter of degree. The view developed above implies that temperature is an important determinant of behavior. This is borne out, for example, by the fact that polystyrene and many other linear high polymers which are typical plastics at room temperature manifest rubbery characteristics at some higher temperature, while natural rubber loses its rubberiness at low temperatures.

Another important implication of the above generalized viewpoint should be noted. Any mass of linear high polymers in which the chains have been oriented into a very high degree of parallelism represents a condition of low thermodynamic probability, *i.e.*, a state of low entropy. Such masses should manifest a general tendency to undergo molecular disalignment and hence shrinkage. That this is indeed the case is shown not only by the retraction of stretched rubber but also by the shrinkage of many textile fibers during scouring and laundering.

Finally it might be well to point out that the same linear polymer that shows the range of properties usually associated with a plastic *before* drawing may become a typical fiber *after* drawing.

COMPARISON OF RUBBERS, PLASTICS, AND FIBERS

233. From the preceding sections it is evident that the main difference between materials of the rubbery and fibrous types is that the former exhibit a small crystallizing tendency while the latter crystallize readily. It is helpful to apply Eq. (2-5) to these systems, remembering that ΔH represents the enthalpy difference between the crystalline and disordered state and ΔS their difference in entropy.

The ΔH term is largely dependent upon the inherent intensity of the secondary valence forces responsible for intermolecular attraction. If the *molar cohesions* are high (Table 2-11), the ΔH term of Eq. (2-5) will tend also to be high and crystallization will be favored. The magnitude of ΔS will depend on the difference in randomness between the disordered and the crystalline states. The $T\Delta S$ term of Eq. 2-5 will therefore depend on the architectural attributes of the chains. Chains that are bulky and unsymmetrical will not fit into a lattice readily and will not crystallize readily even if the intermolecular forces are inherently high. On the other hand, chains that fit readily into an ordered arrangement will tend to crystallize even if the cohesive forces are comparatively weak.

The data of Table 2-11 permit a more quantitative discussion. The last column shows that the typical rubbers, *viz.*, polyisobutylene, polybutadiene, natural rubber, and polychloroprene (neoprene), have specific molar cohesion values of 1 to 2 kcal. These values represent inherently weak secondary valence forces. The materials are mainly hydrocarbon in character. The methyl and methylene segments so prominent in them are of low polarity. Polyethylene represents the exception. This material has more the characteristics of a plastic or fiber in spite of the low intermolecular attractive forces. Because of its exceptional symmetry it fits so readily into a crystal lattice that its tendency is to show fiberlike properties in spite of the weakness of the cohesive forces. Where the specific molar-cohesion values exceed 5 kcal, the substances are typical fibers. Cellulose, the synthetic polyamides (nylons), and silk are cases in point. Finally, where the values lie between 2 and 5 kcal, the materials are plastics. They often exhibit rubbery properties at elevated temperatures and crystallizing tendencies (fiberlike behavior) at normal or subnormal temperatures unless the chain is bulky as in the case of polystyrene.

TABLE 2-12. TENSILE STRENGTHS OF HIGH-POLYMER TYPES
(No fillers or external plasticizers present)

Type of High-polymer Material	Range of Tensile Strengths, psi
Fibers.....	15,000-150,000
Plastics.....	2,000- 15,000
Rubbers.....	300- 3,500

Properties of commercial fibers, plastics, and rubbers will be found in Appendixes B, C, and D, respectively. From these data, the rough correlation contained in Table 2-12 is derived.

THE EFFECTS OF CROSS-LINKAGE

234. The preceding discussion of molecular forces acting in high polymers has been confined to masses of linear molecules where each molecule is discrete and is bridged to its neighbors by secondary valence forces only. But a space polymer is a structure composed of main chains connected to one another by primary-valence cross-links. Obviously, such a structure will behave quite differently.

Continuous flow can occur in a mass only if the molecules can slip completely past one another. *Plastic flow* may be defined as flow that requires a finite starting force. In terms of familiar materials, it is exhibited by pitch, modeling clay, and putty. A mass cannot be molded unless flow can be induced, and a solid can dissolve in a solvent only if the molecules of the solid can be separated from one another. A high polymer is classified as *fusible* if it can be softened by heat sufficiently to exhibit plastic flow without decomposing.

The importance of cross-linkage is now evident. It introduces strong primary-valence restraints. Separation of the main chains of the structure from one another is not possible unless the cross-links are ruptured, a process that can be classed only as chemical decomposition. Solubility, fusibility, flow, and moldability are greatly reduced if not entirely eliminated. As previously stated, even a few cross-links raise the molecular weight enormously, and the kinetic translation of the resulting giant molecules as units is reduced to the vanishing point. For example, if cross-linkage occurs in solution, gelation takes place. The introduction of a large number of cross-links tends to set the mass into rigid, spatial supermolecules of infinite molecular weight. In this sense, a piece of quartz (Table 1-1) is a single molecule; and the larger the piece, the larger the molecule.

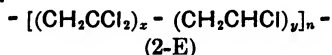
Diamond, mica, wool, and space-polymerized phenol-formaldehyde resin are all cross-linked, but they differ widely in many respects. The physical properties of a space polymer may be considered to depend upon three fundamental structural factors: (1) the character of the main chains; (2) the character of the cross-links; (3) the number of cross-links. In terms of these factors, wool is a space polymer in which the main chains are inherently flexible and extensible, the cross-links fairly long and flexible, and the number of cross-links not very great. We should expect such a structure to be relatively pliable, soft, and extensible; and, while insoluble, it should nevertheless be capable of swelling considerably in

appropriate liquids. This is indeed the case. In terms of the same factors, the diamond represents an extreme of space polymerization. From x-ray diffraction and all other evidence it is incontrovertibly marked as a spatial molecule with each carbon atom linked to four others by primary valence bonds. Theoretically, it should be hard, rigid, and inextensible and should not dissolve or swell even slightly in any solvent. This is in agreement with the facts.

In summing up, we may use the statement previously made in Chap. 1, *viz.*, that linear polymers tend to be soluble, fusible, and moldable, while space polymers incline toward insolubility, infusibility, and nonmoldability, the more so as the degree of cross-linkage increases.

THE EFFECTS OF COPOLYMERIZATION

235. Assume that two monomers, A and B, are individually capable of linear polymerization, and assume further that they may be copolymerized in all proportions. If the percentage composition of the copolymers is plotted against various properties such as tensile strength, softening point, and solubility that depend upon intermolecular forces of attraction, curves similar to those in Fig. 2-13 are obtained in a great many cases. This behavior may be explained readily if one assigns a dominant role to molecular symmetry as a determinant of intermolecular forces of attraction. Thus, "pure" polymer A will have a certain softening point depending upon the attractive forces between its molecules. If a small amount of B is copolymerized with A, symmetry will be reduced and the softening point of the copolymer will be lower than that of pure polymer A. Further increase in B reduces the symmetry and the softening point still more until a composition is reached beyond which increases in B begin to restore symmetry again because the copolymer is approaching pure polymer B in composition. From there on, the softening point rises again. As the softening point decreases, the solubility should and does increase; and the trough of the one curve and the peak of the other are reached at similar percentage compositions. Actual data for polyvinylidene-vinyl chloride copolymers, which have structure (2-E), are presented in Fig. 2-13.



THE EFFECTS OF SUBSTITUTION ON CELLULOSE

236. In Chap. 1 it was stated that, in the case of cellulose, substitution produced effects similar to those of copolymerization. It is instructive to pursue this matter further at this point.

The cellulose molecule is relatively inflexible, and its recurrence symmetry is perfect. Each mer has one primary and two secondary

alcohol groups (Table 1-1). Hydrogen bridging between the chains is very extensive. For these reasons, cellulose, even though it is not cross-linked, is nevertheless insoluble, infusible, and nonmoldable. Neighboring oriented chains are shown in Fig. 2-14a.

Considering any single cellulose mer, a maximum of three substitutions for alcohol groups may be made, and it is possible to have eight different

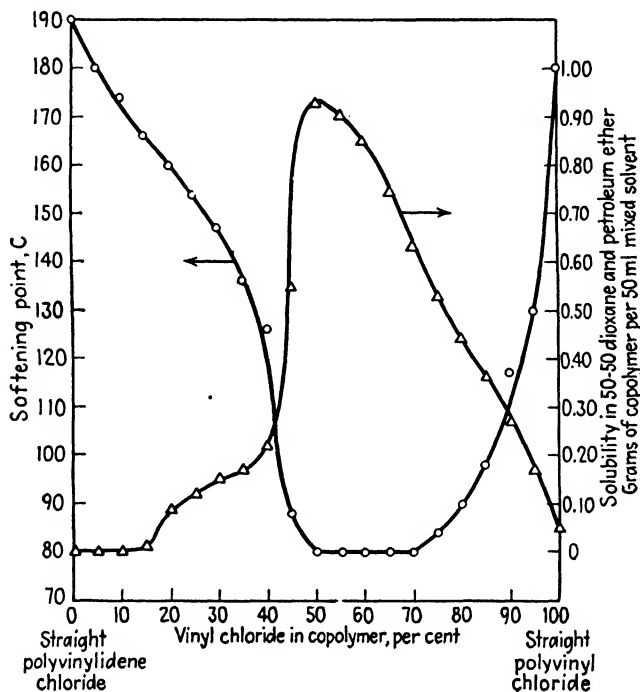


FIG. 2-13. Effect of copolymer composition on softening point and solubility. [R. M. Wiley, U. S. Patent 2,235,782 (1941).]

modes of substitution as follows: complete substitution of all three hydroxyls (D.S. = 3); any of three possible combinations of two substituted hydroxyls (D.S. = 2); any of three alcohol groups substituted singly (D.S. = 1); no substitution whatever (D.S. = 0).

In a chain of many cellulose mers, the D.S. may have any value between 0 and 3.0, including fractional values. The number of possible modes of substitution is astronomical. For example, it has been calculated that on a cellulose chain with a D.P. of 100 and an average D.S. of 1.5, the substituents could be arranged in 10^{89} different ways. One result of substitution is therefore an extensive destruction of recurrence symmetry. Only when substitution is complete can symmetry in this sense be completely restored. Furthermore, the widely used cellulose deriva-

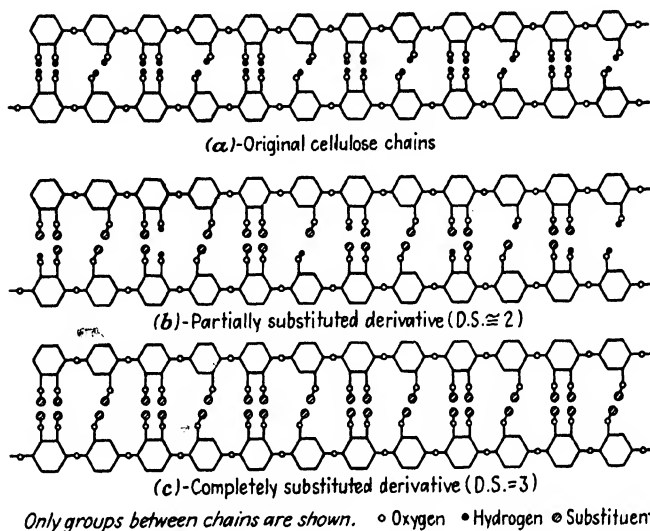


FIG. 2-14. Effects of substitution on cellulose. (E. Ott, in "Chemistry of Large Molecules," Burk and Grummitt, editors, Interscience Publishers, Inc., New York, 1943.)

tives are esters such as cellulose nitrate and acetate and ethers such as ethyl and benzyl cellulose. The substituent groups are less polar than

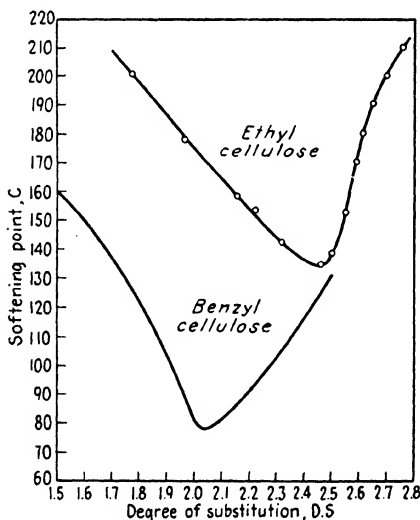


FIG. 2-15. Effect of substitution on softening point. [E. J. Lorand, *Ind. Eng. Chem.*, **30**, 527 (1938).]

the alcohol groups they replace and also bulkier so that the main chains are held farther apart. Architectural symmetry may be still further reduced by substituting two or more kinds of ester or ether groups on the same chains as in cellulose acetate-butyrate. For all these reasons, substitution decreases the attractive forces; and whereas the original cellulose is insoluble, infusible, and non-moldable, the derivatives are soluble, fusible, and moldable with all that this implies. They may be used as plastic binders, surface-coating resins, transparent films, adhesives, and artificial (rayon) fibers.

By varying the degree of substitution, products of different properties are obtained. Figure 2-14a shows oriented unsubstituted cellulose

chains. Figure 2-14b represents a derivative at a D.S. of about 2 with unpaired hydroxyl and substituent groups on chains that are now farther apart. Figure 2-14c represents a fully substituted product at a D.S. of 3. Symmetry has again been restored, but the bridging is weaker than in the original cellulose since the chains are less polar and farther apart. Typical of the changes in properties accompanying these changes in structure are the variations in softening point shown in Fig. 2-15 (compare with Fig. 2-13).

THE DEVELOPMENT OF THE NYLONS

237. The first linear polyesters synthesized by Carothers had average molecular weights of less than 5,000 (Sec. 113). These products could not be spun into filaments.

(The next important advance was the attainment of much higher molecular weights by considerable increase in the time of heating.) Using high vacuum or scrubbing the reaction mass with a stream of nitrogen was important in protecting the reactants from oxidation and also served to remove water of condensation. (Polyesters with average molecular weights as high as 25,000 were produced.) (They were so different physically from their lower molecular-weight analogues that Carothers coined a new name for them. He defined as a *superpolymer* a linear polymer whose average molecular weight exceeds 10,000.) (They were tougher and less soluble, with higher melting points and tensile strengths) than their smaller forerunners. (But what was most important was that they could be successfully spun into fibers.)

In a paper of outstanding significance, Carothers reported on a series of products made by reacting ω -hydroxydecanoic acid, $\text{HO}(\text{CH}_2)_9\text{COOH}$, to different degrees of polymerization. The data are presented in part in Table 2-13. It is seen that, until the D.P. has reached 55, the filaments do not possess sufficient strength to be drawn; appreciable fiber strengths are not attained until the average D.P. is considerably higher. (The low strength of the highest molecular weight product is attributed to less perfect orientation and perhaps decomposition in the fiber mass since it required a high temperature for drawing.)

(The fact that after years of research it was finally possible to produce wholly synthetic fibers was highly gratifying; but, for all that, the results were disappointing. Polyester filaments are of little practical value. Their softening points are so low that they melt at ironing temperatures. They are not strong enough to compete with cotton and silk, and they are not sufficiently resistant to solvents to withstand dry cleaning and laundering.)

In retrospect, it is easy to explain what required years of research to

discover. Carothers finally abandoned the attempt to produce commercial polyester textile fibers. Their shortcomings, enumerated above, are all accounted for on the simple assumption that the intermolecular forces of attraction are not strong enough. The problem, then, is to make linear polymers for which these forces are greater. As discussed earlier, four factors may be exploited toward this end: (1) increase in

TABLE 2-13. PROPERTIES OF POLYMERIZED ω -HYDROXYDECANOIC ACID
 $-\text{O}(\text{CH}_2)_9\text{CO}-$ (MER WEIGHT 170)

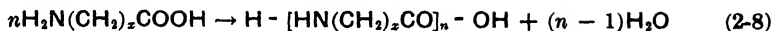
Average M.W. by titration	Average D.P. \bar{n}	Calculated average length of polymer, A	Melt- ing point, deg C	Density d_4^{25}	Spinnability	Tensile strength, psi
780	4.6	60	66-67	1.0957	Absent	
1,720	10.1	123	72-74	1.0935	Absent	
3,190	18.8	188	74-75	1.0877	Absent	
4,170	24.6	313	74-76	1.0814	Absent	
5,670	33.4	440	73-75	1.0751	Very short fibers, will not cold-draw	
7,330	43.2	570	74-75	1.0715	Long fibers but will not cold-draw	Very weak
9,330	55	730	75-76	1.0668	Long fibers that cold-draw	Very weak
16,900	99	1,320	77-78	1.0627	Easily spins and cold-draws	18,600
20,700	122	1,610	77-78	1.0632	Spins with difficulty but easily cold-draws	17,500
25,200	148	1,970	75-80	1.0621	Spins above 210 C and cold-draws	10,000

CAROTHERS, W. H., and F. J. VAN NATTA, *J. Am. Chem. Soc.*, **55**, 4714 (1933).

degree of polymerization; (2) increase in molecular symmetry; (3) increase in degree of orientation; (4) increase in polarity of the mer. In his experiments with polyesters Carothers had about exhausted these potentialities. He had produced streamlined polyesters of high molecular weight and oriented them by elongation under tension, but they were still inadequate.

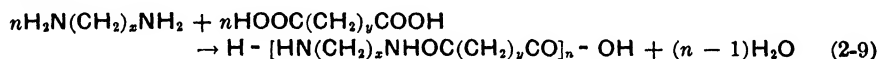
However, it had been known for some time that silk, like other proteins, is a high polymer composed of α -amino acid units. These acids have the general formula $\text{H}_2\text{NCHRCOOH}$ and are thus typical bifunctional compounds capable of polycondensation. Silk is a very strong fiber (Appendix B). Consideration of these facts eventually pointed the way, and Carothers began investigating synthetic polyamides. The first

ones were synthesized in accordance with



When x is greater than 4, cyclization is essentially avoided and a yield of linear polyamide is obtained. In a sense these polymers are simplified proteins. The first one reported was that made from ϵ -aminocaproic acid, $\text{H}_2\text{N}(\text{CH}_2)_5\text{COOH}$. Even at a D.P. of only 10, this nylon has a melting point of 212 C, while the superpolyesters melt at around 80 C. Introduction of the more strongly polar $-\text{CONH}-$ group for the $-\text{COO}-$ group makes the difference. Where the linear polyesters are inadequate, the linear polyamides when cold-drawn make the synthetic fibers of exceptional merit that we now know as the nylons (Appendix B). They are strong, tough, mothproof, and mildew-proof, highly resistant to practically all solvents, and in many respects superior to silk (Chap. 11). Excellent orientation occurs during cold drawing, and intensive hydrogen bridging results similar to that in linear proteins [structure (5-F), p. 213].

Nylons are conveniently manufactured from bi-bifunctional combinations:



Polyhexamethylene adipamide, $-\text{[HN}(\text{CH}_2)_6\text{NHOC}(\text{CH}_2)_4\text{CO}]_n-$ (hosiery nylon), is of this type. (The nylons are designated by the number of carbon atoms in the diamine followed by the number in the dicarboxylic acid; *e.g.*, the above compound is the 6-6 polyamide, also known as *Nylon 66*.) Superpolyamides of this type have melting points ranging up to about 300 C depending on the number of nonpolar methylene linkages in the mer (Table 5-8). Higher melting point is accompanied by higher strength and lower solubility.

The nylons are not merely fiber materials. In the plastics field they occupy a strategic position in that they are thermoplasts of exceptional strength and heat resistance (Appendix C). Whereas most thermoplasts soften in the neighborhood of 150 to 200 F, the polyamides maintain their form stability at operating temperatures up to 350 F, thus competing with thermosetting resins in this respect while maintaining the molding versatility of the thermoplasts (Chap. 8). Nylons are also suitable for making transparent film and wire insulation.

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CHAPTER 3

SOME SPECIAL BEHAVIORS AND PROPERTIES OF HIGH POLYMERS

300. From the previous chapters it is evident that high polymers are governed by the same basic laws as small molecules. Yet, owing to their great size and the fact that they may undergo drastic changes in shape and dimension, some of their behaviors differ considerably from those of low-molecular-weight materials. This is immediately obvious when one tries to manipulate them in plant or laboratory. It is instructive at this stage to discuss the qualitative aspects of certain of these unique behaviors in some detail.

GENERAL QUALITATIVE ASPECTS OF SOLUBILITY

301. The factors influencing solubility are so many and so varied that the development of a completely general, quantitative theory presents an extremely difficult problem. Considerable success has been attained in dealing with systems involving small molecules, and extension of the theory is being made to the field of high polymers; but this progress is hard won, and much territory still remains to be conquered.

302. Empirical Rules. From the mass of available data, mostly relating to small molecules, certain empirical rules have emerged that are very helpful in making qualitative predictions of solubilities. They may be stated as follows:

1. Chemical and structural similarity favor solubility—"like dissolves like." Normal hexane is completely miscible with normal heptane. Aniline is more soluble in benzene and cyclohexane than in normal hexane.

2. Similar polarity favors solubility.

3. Similar internal pressures favor solubility.

The above factors to some extent overlap, since substances of similar constitution are likely to have similar polarities and internal pressures.

4. The higher the melting point of the solute, the lower will be its solubility in a liquid solvent. A corollary to this rule is that the solubility of the solute decreases as the temperature of the liquid solvent is lowered.

5. Solubility decreases as the molecular weight of the solute increases. This is especially true for the solubility of members of a homologous series in a given solvent.

The complexity of solubility relations is reflected in the not unusual breakdown of these rules. To cite just one example, metallic lithium forms partially immiscible liquid systems with the other metals in the same column of the periodic table, *e.g.*, sodium and potassium. Though satisfactory explanations can usually be advanced for such cases, it does not alter the fact that the empirical rules cannot be too strongly relied upon.

In high-polymer systems, the solubility relations grow still more complex owing to such factors as the unusual size of the molecules, the high viscosities of the solutions, and the simultaneous presence of crystalline and amorphous regions in the condensed phase. Nevertheless, the qualitative rules cited above are still useful.

303. Qualitative Approach. A qualitative approach to solubility may be made in the following terms: In a system of solute and solvent, three sets of intermolecular forces of attraction are brought into play, the force of attraction between the solute molecules, the force of attraction of the solvent molecules for one another, and finally, the force of attraction of the solute molecules for those of the solvent. Both the absolute and relative magnitudes of these three forces are important determinants of solubility. The first two tend to keep the solute and solvent separately associated and hence oppose solution, whereas the last force tends to promote solution. The solubility depends upon the *relative* magnitudes of these forces, and it may range from complete miscibility to complete immiscibility.

Consider the case of normal hexane and normal heptane. In this system, solute and solvent are both nonpolar and similar in size, shape, and chemical constitution. The interattraction between hexane molecules is practically the same as that between heptane molecules and consequently equal also to the attraction between hexane and heptane molecules. The attractive forces within and between the two phases are so much alike that it makes little difference whether a hexane molecule is surrounded by other hexane molecules or by heptane molecules, and thus the hexane readily remains dispersed in the heptane, and vice versa. This is a classic example of "like dissolves like."

However, if an attempt is made to dissolve nonpolar hexane in strongly polar water, a hexane molecule cannot remain dispersed between water molecules. The force of attraction among the latter is so strong that they tend to associate by themselves, and the hexane is "squeezed out." Hence, solution does not take place.

Consideration of the forces extant in a system of two strongly polar compounds indicates why irregularity of behavior is frequent. In general, such systems tend to be miscible; but since all three sets of attractive

forces are large, there are many cases in which the forces between one set of like molecules is so much greater than those between the other set or between the unlike molecules that the system may exhibit only partial miscibility. Thus, furfural, a polar molecule with the large dipole moment of 3.57 debyes, nevertheless is incompletely soluble in water.

The important effect that hydrogen bonding may exert on solubilities where polar structures are involved has already been pointed out (Tables 2-9 and 2-10). A quantitative treatment of solubilities will be found in Chap. 6.

304. Specificity of Solvent Action. The highly specific nature of the solvent action of atomic groupings of different polarities and shapes is shown by the behavior of molecules possessing such different groups. These groups contribute their solvent properties independently. Thus 2-nitro-1-butanol exerts the same solvent action as an equimolar mixture of 1-nitropropane and 1-butanol. Again, 2-ethoxyethanol (Cellosolve), $\text{C}_2\text{H}_5\text{OCH}_2\text{CH}_2\text{OH}$, has the solvent properties of both an alcohol and an ether. This behavior is more or less general, although it has been shown that chelation can cause the loss of the independent characteristics of the chelated structures (Table 2-10, page 36).

In practice, the choice between a solvent mixture or a single, multi-structural solvent rests upon various considerations. If a generally high volatility or the selective evaporation of a solvent constituent is desired, mixed solvents are indicated. On the other hand, if low volatility or the maintenance of a constant solvent composition is being aimed at, a multi-structural single solvent might be better.

FACTORS AFFECTING THE SOLUTION AND SWELLING OF HIGH POLYMERS

305. In accordance with what has gone before, one may state the solution process in the following terms: For a solvent to dissolve a mass of solute, the solvent molecules must be capable of penetrating the solute and, by their presence, must sufficiently overcome the attractive forces acting between the solute molecules to enable the latter to separate from one another and diffuse into solution. If the solute consists of very large molecules and the solvent of small molecules, it will be particularly necessary for the solvent to "come to the solute." Because the cohesive forces between high polymers are large does not necessarily mean that they cannot dissolve. If the specific affinity for the solvent is high, solvation and complete dispersion may result. Since intermolecular forces of attraction play such a prominent role in the solution process, it follows that all the factors which determine the magnitude of these forces are determinants also of solubility.

306. Effect of Molecular Weight. For a particular species of linear high polymer, the degree of polymerization is an important determinant of solubility [Eq. (6-26)]. In some cases where the average molecular weight is in the relatively low range of 1,000 to 5,000, solution takes place rapidly and spontaneously, and the resulting solutions are "thin" liquids of low viscosity. Polystyrene, molecular weight 1,000, dissolves quickly in benzene; polyesters, molecular weight 3,000, dissolve rapidly in chloroform. The final solutions are true molecular dispersions but may nevertheless exhibit colloidal behavior if the dispersed chains are large enough. In the higher ranges of molecular weight, 10,000 or more, these same polymers dissolve much more deliberately in the same solvents. The solute mass^{es} undergoes a long, preliminary swelling process during which the chains are being solvated. This swelling is then followed by a gradual breakdown and dispersion of the swollen mass, with the ultimate formation of a solution of high viscosity. Such is the behavior of natural rubber and high-molecular-weight polystyrenes when they are placed in benzene.

This swelling phenomenon is encountered very frequently in high polymers. Indeed, if it is found that a substance swells in certain solvents before going into solution to any considerable extent, this may be taken as almost conclusive evidence that the material is a high polymer.

In Chap. 6 the details of the relation between solution viscosity and degree of polymerization are elaborated. At this point, suffice it to say that the viscosity increases as the degree of polymerization of a polymer solute increases—slowly at first and then much more rapidly (Fig. 2-6). To return to the case of a high-polymer solid being acted upon by small solvent molecules, the solvent must penetrate a mass where the "viscosity" is very high. The process is slow and is accompanied by swelling as the solvent molecules solvate the chains and force them apart. But, even after imbibition, the solvated mass is of high viscosity. The chain molecules, of high molecular weight before solvation, have grown to particles of still greater weight after solvation, in many instances constituting typical emulsoids. Diffusion and dispersion will consequently be extremely slow. Finally it might be mentioned that, if the solute chains are very long or highly branched, purely mechanical entanglement probably contributes to the slowness with which dispersion takes place.

307. Effect of Crystallinity. In some linear-polymeric masses, swelling takes place but actual solution does not follow. In such cases of *limited swelling* the swollen mass comes to equilibrium with the solvent. This indicates that the solvent can solvate and separate the chains at some points but not at others. Crystallinity is one cause for such behavior. Consider a linear-polymer mass with amorphous regions and

well-defined crystallites (Fig. 2-9). It often happens that a solvent can penetrate and solvate the former but not the latter. For example, in the crystallite regions of cellulose all the hydroxyl groups are "paired off" and hydrogen-bonded to one another. Here the intermolecular attractive forces are extremely high, and the structure is dense and impenetrable. By contrast, in the amorphous regions the chains are poorly aligned, and the structure is porous, so that here the hydroxyl groups are comparatively accessible and "free." When the sample is placed in water, considerable swelling takes place. Examination of x-ray diffraction patterns of the swollen mass indicates that the water molecules have penetrated the amorphous regions but have not been able to disturb the crystallites. Hence, swelling takes place, but actual solution does not follow. We have here the interesting concept of a solute molecule being "soluble" at some points along its length but not at others. The study of a large number of cases establishes the fact that, the greater the degree of crystallinity, the less the tendency toward swelling and solution. For example, a cellulosic fiber will swell less in water when it is held under tension. On the other hand, lowering the crystallinity by any means whatever leads to increased swelling and solubility. In most but not all cases where limited swelling is due to crystallinity, it is possible to bring about actual dispersion by raising the temperature or by using a particularly powerful swelling agent.

Crystallinity or orientation also causes the phenomenon of anisotropic swelling (swelling to different extents in different directions). Consider a mass of aligned chains. If this is penetrated by a swelling agent, the chains will be pushed apart laterally and the amount of swelling perpendicular to the axis of orientation will be far more pronounced than that along it. Swelling measurements may therefore afford information regarding molecular arrangement, thus serving as a method of structure investigation. Anisotropic swelling indicates a preferential alignment. Isotropic swelling, on the other hand, indicates either a lack of arrangement of the individual molecules or a random arrangement of crystallites. Typical fibers swell anisotropically, whereas typical rubbers swell isotropically.

308. Effect of Cross-linkage. If main chains are joined to one another by primary-valence cross-links, they cannot disperse independently of one another. The only way to bring about complete separation of the main chains is to rupture the cross-links, but this involves chemical reaction rather than solution. It is a general property of space-polymerized molecules containing any appreciable number of cross-links that they are essentially insoluble in all solvents (see, however, Secs. 408 ff.). Nevertheless, it is still possible for them to undergo limited swelling in

appropriate solvents. How much they actually swell is determined by their three fundamental structural factors (Sec. 234). If the main chains exhibit low crystallizing tendencies and the cross-links are long and few in number, swelling may be considerable. In the opposite extreme represented by the diamond, there are complete insolubility and lack of swelling in all solvents.

It is often possible to destroy cross-links by chemical methods and dissolve the resulting independent chains in a suitable solvent. This affords a method for distinguishing between limited swelling due to crystallinity (secondary valence bridging) and that due to cross-linkage (primary valence bonding). The temperature coefficient of structure disintegration is determined by measuring the time required to obtain the same amount of dissolved material at different temperatures. From this coefficient the activation energy may in turn be calculated. If the latter is high (of the order of 15 to 30 kcal), it may be concluded that solution occurs as a consequence of the rupture of primary valence bonds. This method has been employed to show that the formation of soluble from insoluble pectins and gelatin from collagen involve the rupture of primary cross-links.

309. Effect of Polarity. Since like dissolves like, if a high-polymer solute swells or dissolves in a particular solvent, one may take this as evidence that there are present on the high-polymer chains groups which are similar in polarity or structure to those on the solvent molecules. Thus, if the substance swells in water, formamide, or liquid ammonia, one may conclude that polar hydrophilic groups such as carboxyl, carbonyl, alcohol, or amide are prominent on the chains. However, if it does not swell extensively in such solvents, this does not necessarily mean that polar groups are lacking. Extensive cross-linkage may prevent swelling; or if the degree of crystallinity is high, even chain polymers consisting of pronouncedly polar mers may be insoluble and comparatively nonswelling in polar solvents. Examples are urea-formaldehyde (space polymer), silk (natural polyamide fiber), and nylon (synthetic fiber).

If the polymer will not swell in water or similar polar liquids, still more polar swelling agents may be resorted to, *viz.*, solutions of electrolytes. If the polymer swells or dissolves in these latter without being soluble in water, it may be concluded that the polymer chains are built up of structures with a high dipole moment or that the chains are hydrogen-bonded and the degree of crystallinity high.

By contrast, high polymers built from essentially nonpolar mers will swell or dissolve in relatively nonpolar liquids such as hydrocarbons or halogen derivatives of these. Good examples are the natural and synthetic rubbers.

The polymeric esters constitute an important group exhibiting intermediate characteristics. They swell or dissolve in esters, ketones, and similar solvents of intermediate polarity. Hydrogen bonding is particularly important in this case. Thus, the solubility of a particular sample of polymethyl methacrylate was 77 g per 100 g CHCl_3 and 0.12 g per 100 g CCl_4 .

Finally, it is often found that a chain-polymer solute is more soluble in a mixture of solvents than in the pure solvents individually. This is especially true with chains containing strongly polar groups. The phenomenon may be attributed to one or both of the following effects:

Consider a high-polymer solute containing two kinds of groups differing considerably in polarity. Upon recalling the specificity of solvent action discussed in Sec. 304, it is plausible to envision a situation where a mixture of two solvents will exert a more powerful action than either alone, each of the solvents solvating one type of group on the chains with particular effectiveness. Partly nitrated cellulose is an important case in point [Eq. (1-19)]. This polymer has both $-\text{OH}$ and $-\text{ONO}_2$ groups, and it is found that a mixture of alcohol and ether is a more effective solvent and swelling agent than either solvent alone. In accordance with what has gone before, one might logically postulate that the alcohol exerts the necessary solvating action on the $-\text{OH}$ groups while the ether effectively solvates the $-\text{ONO}_2$ groups. Similarly, there is considerable evidence that acetone solvates only the nitrate groups of a partly nitrated cellulose; thus, fully nitrated cellulose (trinitrate) is soluble in acetone, while the latter is not a good solvent for partly nitrated cellulose unless alcohols are also added.

However, there is a second effect that may also be present. If a chain-polymer solute contains polar groups of one or more kinds and a solvent containing polar groups is added, the more polar parts of the solvent molecules will be oriented toward the polar groups of the chains while the nonpolar parts of the solvent molecules will be directed outward. In other words, the solvated chains will have a less strongly polar surface than the original, and one must not lose sight of the fact that *it is the solvated chains that go into solution*. If it is now found that the addition of a second, less polar solvent enhances the solubility, one might justifiably attribute this to the fact that the second solvent reduces the polarity of the environment to a value more nearly that of the solvated chains. This explanation of the enhanced solvent action of alcohol-ether mixtures on partly nitrated cellulose may be advanced just as logically as that already given. Further aspects of this subject are discussed in Secs. 314 ff.

310. Effect of Chain Flexibility. Assume two aligned chain molecules bridged to one another by secondary valence forces. If the molecules are

flexible, they may be readily separated from one another by a proper solvent. The flexibility permits the detaching of the chains at only one point, followed by subsequent detachment at other points. (This solution process may be compared to stripping of adhesive tape from a surface by lifting and pulling at one end. Not all the adhesion must be overcome at once.) In this case the activation energy of the solution process is small. If, on the other hand, the chain molecules are rigid, their separation by a solvent requires the simultaneous breaking of a large number of secondary valence bridges, a much more difficult process. The magnitude of this flexibility factor may be gathered from the following illustration:

As previously pointed out, cellulose molecules are comparatively rigid. On the other hand, polyvinyl alcohol, $-(\text{CH}_2\text{CHOH})_n-$, is highly flexible. The two substances have the same carbon-hydroxyl ratio. Yet the polyvinyl alcohol molecules are quite soluble in water, while the cellulose is insoluble.

311. Effects of Symmetry. Unsymmetrical polymers often occur naturally or are deliberately produced by the techniques of copolymerization or partial substitution, for reasons already advanced (Secs. 115 and 116). Poor architectural symmetry interferes with packing and crystallization, resulting in more open structures and a general lowering of intermolecular forces, which in turn lead to readier swelling and solution. Poor recurrence symmetry also leaves unbridged groups in "holes," where they are readily attacked by solvent molecules.

To one who is accustomed to think wholly in terms of small molecules some of the effects are at first startling. For example, in dealing with small molecules, when an alcohol is converted to an ether, the solubility in polar solvents ordinarily decreases. Let us consider what happens with the polyalcohol, cellulose. The original chains (Fig. 2-14a) swell but do not dissolve in polar solvents. If we make a partly substituted cellulose ether such as ethyl cellulose, the chains are pushed farther apart and unabridged alcohol groups are left on the chains (Fig. 2-14b). These strongly attract the molecules of a polar solvent. The net result is that partial conversion of the alcohol to an ether *increases* the solubility and swelling in polar solvents. Upon further increase of the D.S. the solubility in polar solvents again decreases until when conversion to the ether is complete it is very slight.

312. Effects of Branching. Various large molecules, especially synthetic addition polymers such as polystyrene, polyisobutylene, polyvinyl acetate, and the polyacrylic esters, while predominantly linear, often show evidences of branching, especially when polymerization is conducted at relatively high temperatures.

Branching may be thought of as changing mainly the shape of the molecule, whereas cross-linkage changes both the shape and the size. It is easy to distinguish between extensive branching and extensive cross-linkage but for obvious reasons difficult to differentiate mild cross-linkage from branching.

Branching alters the shape, producing a molecule that is more nearly spherical and more irregular in structure so that it fits less readily into a space lattice. It therefore exerts marked influences on many properties; *e.g.*, solution viscosity, density, and solvent resistance decrease. Its effect on solubility is often mainly one of altering the *rate* at which solution takes place, whereas cross-linkage very greatly decreases solubility itself.

313. Summary. Studies of absorption, swelling, and solution in liquids may yield considerable information not only on the chemical constitution but also the internal molecular arrangement of high polymers. Conversely, if the chemical constitution and structure of a high polymer are known, application of the qualitative concepts so far discussed will enable many of its properties to be predicted, including its behavior in solvents and swelling agents. Data indicating the applicability of commercial solvents often employed in high-polymer processing will be found in Appendix E.

VISCOSITY, SOLUBILITY, AND GELATION

314. Solvent Action and the Shape of Solute Molecules. Unlike small molecules, high-polymer chains may undergo enormous changes in shape and dimension. A typical high-polymer chain, if fully extended, may have a length some 1,000 times its diameter. Such a chain molecule wriggles, owing to thermal motions; rotations of the individual chain segments occur, and the molecule tends to assume a coiled shape. Secondary valence forces acting between neighboring segments of a balled-up chain tend to keep it so. Strongly polar groups exert a particularly marked effect and may favor internal crystallization of the single molecule into a preferred coil or fold. On the other hand, inflexibility such as that encountered in cellulose reduces the amount of folding or balling.

Consider, now, chain-polymer molecules in solution. One extreme is represented by rather stiff chains in a good solvent. The solvent surrounds each segment with an "envelope" of solvating molecules, which prevents contact with other segments and with other chains. The individual chain is in a relatively elongated condition, and the solvent can stream freely along and around the various parts. Such chains are termed *free-draining*. The other extreme is represented by a very flexible chain in a poor solvent. The chains are irregularly folded into a more

or less tight ball. Considerable amounts of solvent can be immobilized by the entangled segments of the molecule. Such chains are termed *matted-coil*.¹ The state of affairs in dilute solution (0.2 to 1.0 per cent) would be as shown in Figs. 3-1a and 3-1b.

If the concentration were now increased, the chances for chain-to-chain bridging would also increase. The possibility for such association would be greater in a poor solvent than in a good one so that, as shown in

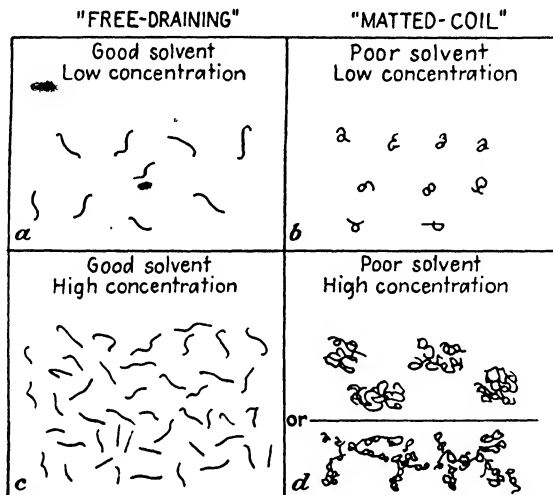


FIG. 3-1. Schematic representation of polymer chains in solution.

Figs. 3-1c and 3-1d, at a concentration where the chains would still be separate and discrete in the good solvent, in the poorer solvent they would have associated into clusters or networks of relatively large size. If this association process were to go too far, precipitation would take place and the mass would gel (lower part of Fig. 3-1d). The important point is the suggestion that high-polymer solute molecules may have different shapes and dimensions in different solvents or even at different concentrations in the same solvent. If this theoretical picture has merit, certain correlations between solubility, viscosity, and concentration should follow. That they do indeed exist will be shown below.

315. Relations between Viscosity and Solubility. The viscosity of a liquid is an internal resistance to flow, a resistance against the slippage of

¹ Chains may often be dispersed in nonsolvents by introducing an appropriate solubilizing or emulsifying agent. The latter affords a surrounding envelope, and the result is a colloidal suspension rather than a solution, as discussed above. At any rate, the dispersed polymer exists as tightly drawn spherical particles, each containing a number of chains but little or no solvent (Sec. 624).

one molecule or layer of molecules past another. The viscosity of a solution depends on many factors, to be discussed at length in Chaps. 6 and 7. Among these are the concentration, size and shape of the solute molecules, and the nature of the solvent.

Large solute molecules offer greater resistance to flow than small ones and consequently increase the solution viscosity to a greater extent so that solution viscosities may be used to measure molecular weights (Sec. 625). It is a common characteristic of high polymers that at concentrations of only a few per cent their solutions are very viscous liquids or even solid gels.

Spherical molecules or particles offer less resistance to flow than elongated ones. An elongated particle rotates in solution and has an effective volume greater than its actual volume. This is not true for spheres, whose effective and actual volumes are equal.

In the preceding section, it was proposed that in a good solvent a chain molecule would be in a more elongated condition than in a poor solvent. It follows that, in dilute solutions, the intrinsic viscosity in a good solvent should be *greater* than in a poor solvent. At high concentrations, however, the chains will tend to associate into larger aggregates. This association will take place more readily in the poor solvent, and a concentration should soon be reached where the resistance to flow has increased greatly owing to the mutual attraction and interference of the chains and large aggregates (Fig. 3-1d). At this same concentration, the good solvent should still be able to prevent chain-to-chain association (Fig. 3-1c), and only the normal increase in viscosity due to increased concentration should result. In other words, *the rate of increase in viscosity with concentration should be distinctly greater in a poor solvent and the viscosity-concentration curves in a good solvent and a poor one should cross one another.* This is indeed the case (Fig. 3-2). If the concentration in either solvent is made high enough, the mass will gel but the gelation concentration is lower for the poor solvent. To summarize, *a good solvent not*

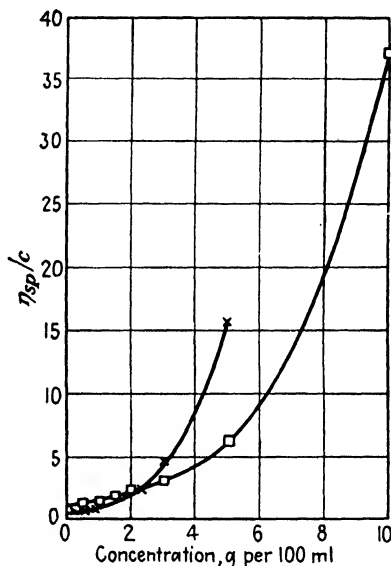


FIG. 3-2. Viscosity-concentration curves of polyvinyl chloride-acetate in a poor solvent, methyl ethyl ketone (x), and a good solvent, cyclohexanone (□). [A. G. Janssen, and B. P. Caldwell, *Polymer Bull.*, 1, 120 (1945).]

only dissolves more polymer but also yields solutions of lower viscosities at higher concentrations.

The above facts are of great theoretical and practical importance. A lacquer is a solution containing one or more high-polymer solutes. In formulating a lacquer mix it is desirable to have, at one and the same time, as high a concentration and as low a viscosity as possible. The former is required to get a surface coating film of suitable thickness, while the latter is necessary if the solution is to be brushed or sprayed readily. The proper choice of solvent is thus of great consequence. Extensive measurements not only have confirmed that solvents having the highest solvent power give the lowest solution viscosity but also show that the correlation is so good that solvent power may be reliably predicted from solution-viscosity measurements.

For reasons previously indicated, mixed solvents are usually best for polymers having groups of more than one type or degree of polarity. Cellulose nitrate for lacquers is only partially substituted (D.S. ~ 2.25) and contains both alcohol and nitrate groups. Measurements on 5 per cent solutions of this polymer in ethyl acetate-ethyl alcohol or butyl acetate-ethyl alcohol mixed solvents show that additions of alcohol up to 40 to 60 per cent by volume increase the solubility and lower the viscosity, while greater additions cause the solubility to drop and the viscosity to rise again. Commercial ethyl cellulose lacquer polymer contains both ether and alcohol groups. The effects of solvent composition are shown in Fig. 14-1, page 606.

Another method widely used to evaluate solvent power is the following: The high-polymer solute is dissolved in each of various solvents that are to be compared, all the solutions being made one standard strength. Then, for each solution, a determination is made of the amount of some nonsolvent that must be added to cause initial precipitation. This is known as the *dilution-ratio method*. Presumably, the solvent to which the largest amount of nonsolvent (diluent) may be added before precipitation occurs is the most powerful.

The weakness of the dilution-ratio method from the theoretical standpoint lies in the fact that the first additions of the diluent may actually improve the solvent power of the medium, for reasons previously indicated. However, the determination is of great practical value in the economic evaluation of solvents since it affords a direct measure of the extent to which more expensive solvents may be replaced by less costly latent solvents and diluents. This method is to a considerable extent replacing evaluation by the viscosity-measurement method.

316. Gelation Phenomena : Thixotropy. Gelation caused by primary-valence cross-linkage in a polyfunctional system is irreversible. In this

case the continuous macromolecular network, which causes immobilization of the mass, is held together by primary valence bonds and, once formed, can be broken only by drastic treatments such as thermal decomposition. However, this is just one kind of gelation. In many cases, when a linear-high-polymer solute is dissolved in a solvent, a solution is obtained that sets to a gel when left undisturbed. The gel is readily broken by simple stirring or shaking but reforms on standing. This interesting phenomenon is called *thixotropy* and is a reversible, isothermal change in consistency induced by mechanical shear.

A thixotropic gel can also be broken merely by adding a second solvent of appropriate character. If too much of this solvent is added, the solute precipitates as a separate phase. When a thixotropic gel has formed, it is usually possible to leach out a considerable portion of the solute chains without breaking down the gel structure. Finally it should be mentioned that many such gels show a tendency to densify slowly on standing, with attendant sweating or squeezing out of solvent as a separate phase, this latter phenomenon being known as *syneresis*.

Obviously, a thixotropic gel is quite different from a space-polymer gel. From the evidence, it is a weak structure held together by secondary valence bridging. At any rate, it may be very satisfactorily explained as follows: Assume, for illustration, that a small number of widely separated polar groups are present on an essentially nonpolar chain-polymer solute. This polymer will dissolve in a nonpolar solvent, and, at a proper low concentration, a liquid solution will form. As the solute chains move about, some of the widely separated polar groups will eventually find one another and bridge. If conditions are right, a continuous, dendritic, structural framework will form and the mass will eventually gel. The structure will be weak, and simple stirring or shaking may be sufficient to pull apart the associated polar groups, thus destroying the gel framework and causing the mass to liquefy. This process could be repeated many times.

If a proper amount of polar solvent is now added, it will solvate the polar groups and prevent them from bridging. This, in turn, will prevent gelation. However, if too much of this solvent is introduced, the chain-polymer solute, which we have postulated as being predominantly nonpolar, will be insoluble in the medium and will precipitate as a separate phase.

When the thixotropic gel first forms, the consistency rises to its abnormally high value. This hinders diffusion and makes it difficult for additional solute chains to become attached to the gel framework. It will thus be possible to leach out these solute chains with solvent. However, on prolonged standing, many solute chains will eventually be able to

associate with the framework, thereby drawing the structure more firmly together with the attendant expulsion of solvent (syneresis). Thus every behavior of the thixotropic gel has been accounted for in simple theoretical terms.

The thixotropic effect need not involve a change from sol to gel, which may be considered as an extreme manifestation. It may involve merely a change from less viscous to more viscous liquid. At any rate, all thixotropic systems are readily disturbed by small forces, and it may well be that in all cases there are involved the formation and breakdown of a weak, continuous framework of dispersed particles whether they be high-polymer molecules, colloiddally dispersed droplets, or finely divided solid particles. The matter is dealt with at greater length in Chap. 7. At any rate, thixotropic effects are very common in high-polymer and colloidal systems, and their great practical importance may be gathered from the following examples.

It is now known that the hydrocarbon chains of natural rubber (Table 1-1) carry a small number of polar groups, either present originally or formed by oxidation during preparation or mastication (Sec. 1303). Rubber cement may be made by dissolving rubber in a hydrocarbon solvent such as naphtha. Ordinarily not more than a few per cent can be dissolved without obtaining a gel or a solution too high in viscosity to permit of proper spreading or brushing. It is essential to be able to dissolve more rubber and at the same time keep the viscosity low enough for easy application. This desirable result is obtained by adding a proper amount of polar solvent, alcohol, which reduces the thixotropic effect in accordance with previous discussion. Quantitative data are shown in Table 3-1. Note that effectiveness of the alcohols decreases as their polarity decreases.

Thixotropy is highly desirable, if not absolutely essential, in surface coatings and some greases (Sec. 719).

TABLE 3-1. REDUCTION OF VISCOSITY OF RUBBER-BENZENE SOLUTIONS BY THE ADDITION OF ALCOHOL

(Amounts of alcohol shown below are added to 15 ml of a 1 per cent solution of rubber in benzene)

Alcohol	Methyl				Ethyl				Amyl			
No. of ml added.....	0	1	2	3	0	4	4.5	5	0	15	17	18
Solution viscosity.....	94	58	44	ppt	94	43	37	ppt	94	55	49	ppt

PLASTICIZATION

317. Definitions. Plastic flow is flow that requires a finite starting force. Polystyrene and other synthetic plastics are received by the

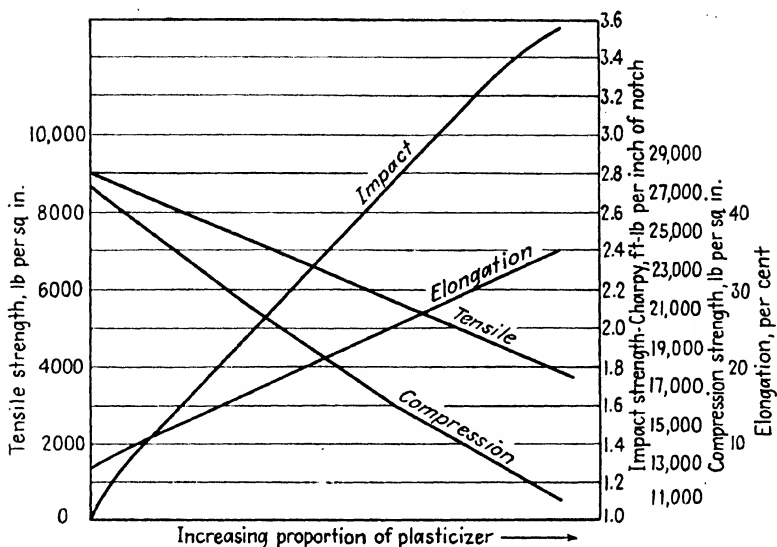


FIG. 3-3. Plasticizer content and physical properties of cellulose acetate. (J. Delmonte, "Plastics in Engineering," Penton Publishing Company, Cleveland, 1942.)

molder in the form of powder, flakes, or granules. To mold these materials into a finished article of desired shape and dimensions it is necessary to induce flow by applying heat and pressure to the material while it is in a mold. The *plasticity* of a material may be defined as the degree to which it will exhibit plastic flow. A *plasticizer* is a material that increases the plasticity of a mass. In broader terms, a *plasticizing agent* is anything that increases the plasticity. Plastic flow may be induced in an otherwise rigid mass merely by raising the temperature. Hence heat is a widely employed plasticizing agent. Plasticization increases the softness, flexibility, and extensibility and decreases the yield point, modulus of elasticity, and tensile strength (Figs. 3-3 and 3-4). In other words, plasticization increases the mobility and brings the mass nearer to the liquid state. For continuous flow to take place it

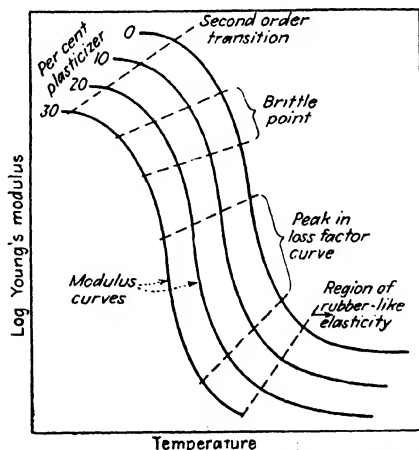


FIG. 3-4. Generalized effect of plasticizer content and temperature on properties of high polymers. [R. F. Boyer, and R. S. Spencer, *J. Polymer Sci.*, **2**, 157 (1947).]

is essential that the molecules be able to move with respect to one another. In theoretical terms, the ease with which this relative motion occurs depends on the strength of the cohesive forces acting between the molecules. Hence, a plasticizing agent is anything that reduces or overcomes intermolecular forces of attraction.

318. External Plasticization. An external plasticizer is a material that imparts plasticity to a mass primarily by exerting solvent action. If this action is extensive and too large an amount of solvent is added, the mass is reduced to a liquid devoid of mechanical strength. If, on the other hand, the solvent action is not too marked and smaller amounts of the solvent or plasticizer are added, a highly viscous liquid or solid of somewhat rubbery properties and considerable mechanical strength may result. From these considerations one would be led to predict that, as plasticizer is added to a linear-polymer mass, softening point and tensile and compressive strength would decrease, while extensibility, pliability, and the ability to absorb impact would increase. That this is indeed the case is illustrated by the experimental data of Fig. 3-3. In some operations a plasticizing action is desired that is temporary only. For this purpose a highly volatile solvent may be used as plasticizer. For example, the high-polymer constituents of a lacquer are dissolved in volatile solvents to form a solution of low enough viscosity to permit ready spraying or brushing over a surface. When the solvents evaporate, the plasticizing effect goes with them and the liquid changes to a solid surface coating of requisite hardness and mechanical strength.

But in many commercial products a *permanent* plasticizing effect is required. When such is the case, an external plasticizer employed for the purpose must not evaporate. It must stay in the finished product, or the properties of the latter will revert to those of the unplasticized material. For example, polyvinyl chloride, $-(CH_2CHCl)_n-$, is a typical plastic of considerable rigidity. By the incorporation of suitable amounts of tricresyl phosphate, a mildly polar, high-boiling liquid, the mechanical properties are downwardly revised to those of a material which can be used as a nonrigid plastic. The plasticizing effect is shown in Table 3-2.

TABLE 3-2. EXTERNAL PLASTICIZATION OF POLYVINYL CHLORIDE BY TRICRESYL PHOSPHATE

Tricresyl phosphate, wt. %	Tensile strength, psi	Elongation at break, %
0	5,690	2
30	3,840	170
60	1,000	500

Although many secondary properties may be required, the basic attributes of a good permanent external plasticizer are (1) that it be compatible with the material it is to plasticize and (2) that it be non-volatile. It is desirable that the solvent action it exerts be neither too strong, in which case there would be a tendency for the plasticized product to be fluid rather than rubbery, nor too weak, in which case it would not be "compatible" with the material being plasticized. As used in this field, *compatibility* means the ability of two or more constituents to mix and remain homogeneously dispersed in one another. This implies a certain mutual affinity (solubility) of the several molecular species for one another. If a compound is to be used as a commercial plasticizer, it is likewise desirable for it to be compatible with as many different high polymers as possible. Now, if it were a very strongly polar material, it would not be compatible with nonpolar molecules, and vice versa. Appendix E contains information on various types of commercial plasticizers. It will be noticed that they are almost all liquids of high boiling point, *i.e.*, negligible vapor pressures at room temperature. This differentiates commercial "plasticizers" from commercial "solvents." Furthermore, they are practically all esters. This is no accident. The polarity and symmetry of the esters are such that the intermolecular forces of attraction are neither very high nor very low. They will therefore tend to exhibit satisfactory compatibility with a wide variety of molecules.

There is an important group of materials called *nonsolvent plasticizers*. They are so designated because at use temperature they are not sufficiently miscible with the high-polymer binder to form a truly homogeneous phase. Rather, the mass consists of two phases, (1) plasticizer-rich microdroplets composed of a solution of the lower molecular-weight fractions of the binder in the plasticizer enmeshed in (2) a plasticizer-poor continuous network formed by the larger, almost insoluble molecules of the binder. At molding temperatures, however, the binder and plasticizer are completely miscible. The term "nonsolvent" plasticizer is thus somewhat of a misnomer.

Such a material has certain advantages: it tends to be flexible and yet possessed of high strength at the use temperature; it tends to resist embrittlement (remain flexible) at subnormal temperatures; and, finally, it flows and molds readily at elevated temperatures. A disadvantage compared with products containing ordinary plasticizers is a more pronounced tendency toward expulsion or separation of the plasticizer under the action of mechanical stress or temperature change.

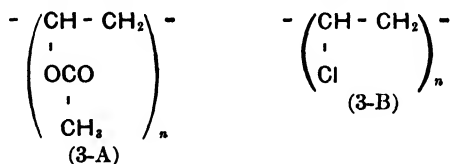
As a class, external plasticizers that are intended to be permanent have the following shortcomings: They may be lost by slow evaporation,

they may bleed out of the product, or they may be leached out by solvents. To minimize these shortcomings, there is a distinct trend toward the employment of compounds with molecular weights of 1,000 to 3,000 in place of those running molecular weights of 100 to 300. Synthetic *low* polymers are often found suitable for the purpose.

From Fig. 3-3 and Table 3-2 it is evident that the changes in physical properties which can be effected by external plasticizers are very extensive. But since this effect is essentially a solvent action, it follows that cross-linkage will reduce the amount of modification that an external plasticizer is capable of producing. Just how much it can do will depend on the number and length of cross-links. External plasticizers exert only minor effects on highly cross-linked structures. To modify the properties of the latter and thus extend their range of usefulness, recourse is had to the incorporation of an entirely different class of compounding materials known as *reinforcing fillers*. Whereas the modifications effected by plasticizers are in the direction of mechanical weakness, those produced by reinforcing fillers are more in the direction of mechanical improvement. Reinforcing fillers will be discussed at length in later chapters.

319. Internal Plasticization. Since plasticization has been revealed as a process that reduces intermolecular attractive forces, it follows that copolymerization and cellulose substitution are plasticizing agencies and that the effects discussed in Secs. 235 and 236 are typical results of plasticization. Nitrate groups plasticize cellulose [Eq. (1-19)]. Styrene units plasticize and enhance the rubberiness of buta S [Eq. (1-17)]. The plasticizing structures become a chemical part of the polymer structure. Consequently, unlike external plasticizers, they cannot be lost by evaporation, bleeding, or leaching. Their effect is permanent and is called *internal plasticization*. Branching also results in internal plasticization.

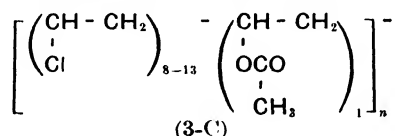
A widely quoted example of internal plasticization is that of vinyl chloride by vinyl acetate. Polyvinyl acetate [structure (3-A)] is so soft and mechanically weak and has such poor resistance to water and solvents in general that it is not suitable as a fiber, plastic binder, or rubber. Its



properties limit it to a few uses such as a component for adhesives or external plasticizer for certain other polymers. On the other hand, polyvinyl chloride [structure (3-B)] is a strong, tough, hornlike plastic with excellent resistance to water and hydrocarbon solvents. But like polyvinyl

acetate its uses are greatly limited. A main reason is that it cannot be molded per se because its molding temperature is perilously close to its decomposition point.

It might be thought that these two polymers, whose individual applications are so highly limited, could be used to externally plasticize one another, but this is not the case, for they happen to be incompatible. However, by copolymerizing smaller amounts of vinyl acetate with larger amounts of vinyl chloride, internal plasticization occurs, and a whole series of commercially useful polymers result [structure (3-C')].



Helped along a bit by a heat stabilizer (Sec. 804) one of these polyvinyl chloride-acetate resins can be very successfully injection-molded into

TABLE 3-3. VINYL CHLORIDE-ACETATE COPOLYMERS. CORRELATION BETWEEN COMPOSITION, MOLECULAR WEIGHT, AND APPLICATIONS

Item	Wt. % of vinyl chloride	No. of chloride mers per acetate mer	Range of average M.W.'s	Typical applications
Straight polyvinyl acetate	0	0	4,800-15,000	Limited chiefly to adhesives
Chloride-acetate copolymers	85-87	8-9	8,500-9,500	Lacquer for lining food cans; sufficiently soluble in ketone solvents for surface-coating purposes
	85-87	8-9	9,500-10,500	Plastics of good strength and solvent resistance; molded by injection
	88-90	10-13	16,000-23,000	Synthetic fibers made by dry spinning; excellent solvent and salt resistance
	95	26	20,000-22,000	Substitute rubber for electrical-wire coating; must be externally plasticized; extrusion-molded
Straight polyvinyl chloride	100	Limited, if any, commercial applications per se; nonflammable substitute rubber when externally plasticized

useful plastic articles. Not many acetate units are required, and the desirable properties of the chloride are in large measure retained. Indeed, by varying the ratio of chloride to acetate units between 8:1 and 13:1 and at the same time varying the average molecular weight between 8,000 and about 25,000, copolymers suitable for such widely divergent items as lacquers, plastics, and synthetic fibers are produced. For any given copolymer the plot of molecular weight (or D.P.) vs. mechanical and physical properties follows the usual form (Figs. 2-5 and 2-6). By calling on external plasticizers (Table 3-2) the range of usefulness may be extended still further to include substitute rubber. Thus, from two monomeric raw materials, polymers for almost every major field of application may be made by applying the fundamental techniques of internal and external plasticization and molecular-weight control (Table 3-3).

The student should recognize that this is indeed the "tailor making" of molecules. By controlling the average molecular weight, they are cut to length. By varying the copolymerization ratio, they are made to pattern to suit the needs of the individual customer.

THERMAL BEHAVIOR

320. Mention has already been made of the existence of crystalline and amorphous regions in chain-polymer masses. X-ray evidence indicates that long-chain molecules pass continuously through alternate amorphous and crystalline (micellar) regions. For example, in native cotton the average length of the crystallites is of the order of 600 to 1,000 Å, while that of the individual molecules as determined by various molecular-weight methods is at least 10,000 to 18,000 Å.

It seems that long molecules exhibit a marked tendency toward polymorphism. Thus, three or more modifications have been found in the case of cellulose, and two are known for gutta-percha; two or three exist in fully acetylated and fully nitrated cellulose. In some instances, these allotropic modifications are attributable to changes in the arrangement of the chains with respect to one another in the lattice; in others, they appear to reflect changes in the internal crystallization of the individual chains, for example, changes from a planar zigzag to a helicoidal shape. As the temperature is varied, phase changes are rather frequently encountered (Secs. 515 ff.).

321. Melting Points. Relatively few high-polymer materials exhibit sharp melting points in the ordinary sense. Many exhibit broad softening zones and still others do not melt at all but finally reach a temperature at which charring or decomposition takes place.

Several reasons may be advanced for this general lack of sharp melting points. Chain polymers are never all of the same size (Fig. 1-2). The mass is at best a mixture of many molecular sizes. Absorbed impurities are almost invariably present. Furthermore, even in the best crystallized polymeric masses there are always amorphous or glassy regions in which the molecules are in disorder suggestive of the liquid state.

Consider a solid high polymer whose molecules consist to a large extent of nonpolar segments with only occasional strong attractive centers along the chains. Assume that the symmetry of the chains is poor and that the crystallinity is of a very low order. These are essentially the conditions encountered in a typical rubber. Long-range interaction and purely mechanical entanglement may prevent the relative motion of one whole chain with respect to the others, but the nonpolar segments may still be capable of local motion since they are not tightly bridged to one another. In other words, *external* mobility of whole chains is not probable, but *internal* local mobility of chain segments still exists. If the temperature drops below the second-order transition (Table 5-9, page 188), even the internal motions are frozen in and the mass is a "glass," i.e., a brittle material of high consistency (greater than about 10^7 poises). If the temperature is now raised gradually and brought above the transition point, the weak secondary forces acting between the nonpolar chain segments are overcome and the internal mobility of these segments becomes manifest. The mass is now a rubbery solid (Fig. 3-4). Finally, if the temperature is raised high enough so that the attractive forces at the points of strong bonding are also overcome, external mobility of the chains as a whole results and the mass exhibits the properties of a viscous fluid. It is then molten. Since the temperature range that must be traversed to bring about these changes may be considerable and the initial, intermediate, and final stages are woefully lacking in the crystal organization associated with true solids, there is no melting point but rather a very broad softening zone.

Comparatively sharp melting points are in general exhibited only by polymers of strong crystallizing tendencies. The linear polyesters and polyamides (nylons) synthesized by Carothers are highly symmetrical. At molecular weights below 5,000 their crystallinity is readily observed under an ordinary microscope, and they melt sharply like ordinary small-molecule crystals. The same polyesters, when polymerized to average molecular weights of above 10,000, do not appear crystalline under the microscope but at room temperature exhibit sharp x-ray powder diffraction patterns closely resembling those of their lower molecular weight analogues. Upon heating, they "melt" at approximately the same temperatures as the latter, but the melting phenomenon is quite different.

At the "melting" point there is a sharp change from an opaque material with a well-defined x-ray pattern to a transparent mass whose x-ray pattern is a diffuse halo characteristic of a liquid. However, a tendency to flow is not observed until the temperature is raised considerably above this transition point. It is obvious that what is considered the melting point in such cases will be a matter of definition or will depend on the method of observation.

If the chains of a linear-polymer mass are too firmly bonded or the crystallizing tendencies are too high, rupture of primary bonds may result before thermal agitation can overcome the forces acting between the chains. In such cases thermal decomposition will take place before a melting point is reached. Primary-valence cross-linkage leads to the same result. Before external mobility of the main chains is possible, rupture of the cross-links must occur.

Hydrocarbon materials in general have low "melting" points because the specific molar cohesions are low (Table 2-11), ranging from 1 to 2 kcal. As noted in Sec. 233, an exception is polyethylene. For this polymer the molar cohesion is only about 1 kcal, but the chains possess the highest possible symmetry. It seems that, upon melting, these chains rotate and oscillate vigorously; but, because of their exceptional symmetry, the segments still remain parallel in small volumes in a "liquid crystal" structure. The gain in randomness between the molten and crystalline states is small, that is, ΔS is small, so that the material has a surprisingly high melting point (around 120 C), melts fairly sharply, and exhibits physical properties more characteristic of plastics and fibers than of rubbers. This subject is dealt with at greater length in Sec. 517.

When the specific molar cohesion is high (above 5 kcal), linear polymers are typically fibrous. If they melt at all, the melting points are generally high. Thus, Nylon 66, a synthetic polyamide fiber (Table 1-1) melts sharply at around 260 C.

322. Flow Temperatures, Softening, and Deformation under Heat. Manufacturers and users of high-polymeric materials are vitally interested in the temperatures at which they may be successfully molded and also the temperatures at which finished products will soften and distort under load to a serious extent. "Softening points" as reported in the literature at the present time are not very helpful since they vary with the conditions and methods of test. Since melting points are likely to be indefinite or entirely devoid of significance, standard test procedures are used to describe the thermal behavior of the materials in practical, meaningful terms. Two of these will be described briefly at this point as an illustration of how a property difficult to define is translated into measurable terms.

Test for Measuring Flow Temperatures of Thermoplastic Molding Materials (A.S.T.M.¹ Standard D 569). A cylindrical test specimen, $\frac{3}{8}$ in. D by $\frac{3}{8}$ in. H , is slid into place in a close-fitting, hot charge chamber, which opens into an orifice $\frac{1}{8}$ in. D by $1\frac{1}{2}$ in. L . The temperature of the chamber is controlled to ± 0.5 C, and a ram applies a pressure of 1,500 psi to the test piece for 2 min ± 1 sec. The distance to which the material under test has flowed into the orifice is measured. Runs are made at three or more temperatures to get flows ranging from 0.5 to 1.5 in. The logarithm of the flow is then plotted vs. temperature. The points fall on a straight line. The temperature for which the flow is exactly 1.0 in. is read off and reported as the flow temperature.

Test for Deformation of Rigid Plastics under Load (A.S.T.M. Standard D 621). A $\frac{1}{2}$ -in.-cube test specimen is conditioned and then placed between parallel plates. A constant force system applies a fixed force for a period of 24 hr while the temperature is maintained constant. The per cent deformation (shortening) of the test piece is reported.

323. Behavior Classification of High Polymers. From the standpoint of manufacturing and fabrication, one of the most useful properties a structural material can have is the ability to exhibit plasticity and continuous flow under proper conditions of temperature and pressure. If it has this property, it may be formed to almost any desired shape by the application singly or together of heat and pressure and by means of such techniques as casting, rolling, pressure molding, extruding, and drawing under tension. On the other hand, if it lacks this property, it can be shaped only by more costly operations such as drilling, turning, sawing, and routing.

It is helpful to divide high polymers into three categories in accordance with their behavior on the application of heat and pressure.

324. Thermoplastic Polymers: Thermoplasts. Polymers of this group, either per se or with suitable plasticizer, exhibit continuous flow under the influence of heat and pressure. *The change from solid at room temperature to plastic solid or viscous liquid at high temperature is reversible.* Like sealing wax, a thermoplast can be resoftened and reshaped almost any desired number of times. *A thermoplast is both soluble and fusible.*

Thermoplastic polymers may be linear or branched but, at most, only mildly cross-linked. Cellulose esters and ethers, unvulcanized natural rubber, linear polyamides and polyesters, vinyl addition polymers such as polystyrene, polymethyl methacrylate, and polyvinylidene chloride, and linear silicones are typical examples.

¹ American Society for Testing Materials. This is the most important American organization for developing standard methods of test for engineering materials.

325. Thermosetting or Heat-hardening Polymers: Thermosets. A thermosetting polymer is originally fusible. Upon the application of heat and pressure it passes through three successive steps, fusion, flow, and hardening. These transformations end in the formation of an *insoluble, infusible solid*. The process is irreversible. Like portland cement, once hardened, a thermosetting material is no longer fusible or moldable.

So far as is known, cross-linkage accounts for this "setting." Obviously, a thermosetting polymer must enter the shaping process in the form of linear, functional molecules and emerge as a cross-linked space polymer. This means that, while it is in the mold, chemical reaction is taking place in a polyfunctional system.

For several important kinds of thermosetting resins, three molecular stages are recognized and often referred to in the literature, although the classification is somewhat arbitrary without sharp dividing lines between the three stages. *A-stage resin* consists of comparatively short, linear, functional molecules that are fusible and soluble in suitable solvents. *B-stage resin* is composed of longer chains, i.e., the D.P. is higher, but the molecules are still functional and essentially linear with few if any cross-linkages. Although B-stage resin may be practically insoluble, it is still fusible. *C-stage resin* is so extensively cross-linked that it is permanently insoluble and, to all intents, infusible.

Important examples of thermosetting materials are A- and B-stage phenol-aldehydes, urea-aldehydes, and melamine-aldehydes, certain polyesters such as the glyptal resins, certain silicones, and mixtures of rubber with sulfur or other vulcanizing agents (Table 1-4, page 16).

326. Nonmoldable Polymers. Nonmoldable polymers are those which cannot be induced to exhibit continuous flow without decomposition, either per se or with plasticizer added. In this category are found all highly cross-linked polymers, some mildly cross-linked polymers like soft-rubber vulcanizates, and some purely linear polymers like asbestos and cellulose in which the secondary valence bridging is exceptionally strong. *Nonmoldable polymers are insoluble and infusible*. From what has gone before, it is obvious that a typical thermoset starts its career as a thermoplast but during molding is converted to the nonmoldable category.

327. Remarks on Behavior Classification and Manipulation of Mixes. The behavior classification of a polymer is a very important item. One of the first points of information desired is whether a polymer is thermoplastic, thermosetting, or nonmoldable. The reason is obvious. With one word an immediate indication is given of the structure and physical properties of the polymer, the methods of molding and shaping to which

it will or will not lend itself, and the general character and properties which the finished product is likely to possess.

Curves 1 and 2 of Fig. 3-5 represent the idealized thermal behavior of the moldable types of polymers. The classification is somewhat arbitrary since, among other things, nothing has been stated regarding the factor of time. To appreciate this one has only to assume that a certain fusible material heat-hardens extremely slowly. Would it be classed as a thermoplast or a thermoset? A few materials, notably shellac, do indeed exhibit thermal behavior of an intermediate nature represented schemat-

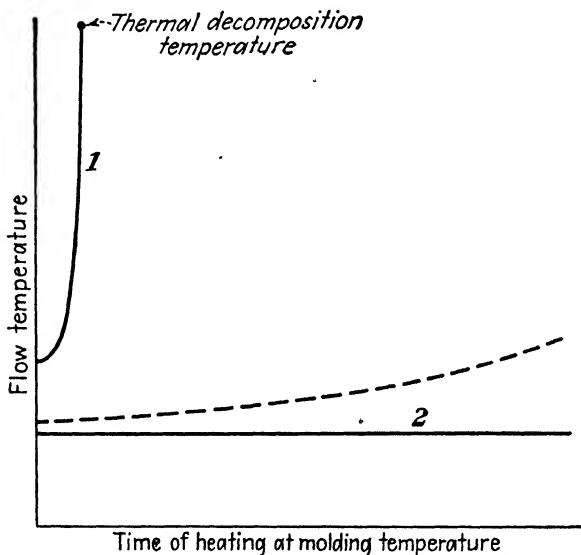


FIG. 3-5. Generalized thermal behavior of moldable high polymers. Curve 1: typical thermosetting material. Curve 2: typical thermoplastic material.

ically by the dotted line of Fig. 3-5, and resins can be prepared that set slowly or rapidly. Furthermore, it is possible to start with sheets of thermoset phenol-aldehyde materials and, by heating them rapidly to a high temperature and then applying stress, to form them into curved shapes. The process is known as *postforming* (Sec. 854). The fact that the thermal-behavior classification is somewhat arbitrary does not detract from its usefulness or importance. The point is that the reader should not regard it as something absolute.

Depending upon their structure and mechanical properties, linear polymers may be classified into rubbers, thermoplasts, or fibers. Mechanically speaking, the effect of cross-linkage is to produce a nonmoldable fourth type of material that is often not a rubber or a plastic or a fiber. The term *thermoset material* is inadequate since in many cases, such as

the drying of oleoresinous varnishes, cross-linkage occurs without the application of heat. The term *mutaplast* is here suggested and will be used in this text to describe a material, originally thermoplastic, that, during industrial manipulation, has been converted or mutated to an insoluble, infusible form by any technique or mechanism whatever. Thus, it will embrace not only heat-hardened resins but also dried varnish films, cold-vulcanized rubbers, etc.

So-called 'rubber' products and plastic products very seldom contain rubber or plastic alone. Almost invariably, they are made from a *mix* containing four to ten materials, the rubber or plastic serving as the *binder* that cements the mix into a cohesive finished product. The auxiliary materials are known collectively as *compounding ingredients* and embrace such items as plasticizers, reinforcing fillers, coloring materials, vulcanizing and hardening agents, and aging inhibitors (Secs. 801 *ff.*). Without them the finished product would be inferior or even useless. For good results, the compounding ingredients must be intimately mixed with the binder before the molding operation is reached. Then during molding the binder must be capable of fusion and flow in order that a strong, coherent product may form. It follows that a thermosetting (mutating) binder must be manufactured in a linear-polymeric, sufficiently fusible, moldable condition and must be in that condition when it is mixed with compounding ingredients prior to molding. If it were introduced into the mix in its space-polymerized mutaplast stage, it would not be able to fuse, flow, and bind the product.

When a thermoplastic binder is being employed, scrap, trimmings, and imperfect pieces may be ground and remolded. This cannot be done when a thermosetting binder is used.

MECHANICAL PROPERTIES

328. Effects of Molecular Structure. When a test specimen is pulled apart, bent, or otherwise deformed, work is being done against intermolecular forces of attraction. Our ultimate goal is to be able to calculate quantitatively the strengths of a material from a knowledge of its chemical composition and its molecular and gross architecture. That goal is still far distant although some progress is being made toward it.

The broader aspects of the relations between mechanical behavior and molecular structure and chemical constitution have already been outlined. Whether a polymer is a rubber, plastic, fiber, or mutaplast and whether it is thermoplastic, thermosetting, or nonmoldable depend upon various structural and chemical factors. Table 3-4 is a qualitative summary of current knowledge of the subject.

TABLE 3-4. RELATION BETWEEN PROPERTIES AND STRUCTURAL AND CHEMICAL CHARACTERISTICS OF HIGH POLYMERS

Property	Average degree of polymerization	Branching	Cross-linkage	Non-polar structures	Polar structures	Flexibility of chains	Readiness of chains to crystallize	Orientation of crystallites
Modulus of elasticity.....	+	?	+	?	?	-	+	+
Ultimate tensile strength.....	+	?	?	-	?	?	+	+
Ultimate impact strength.....	+	?	-	+	?	+	-	-
Elongation at break.....	+	?	-	+	?	+	?	?
Range of reversible extensibility.....	+	-	-	+	?	+	+	?
Tendency to contract.....	+	?	-	+	-	+	+	?
Surface hardness.....	+	?	+	-	+	-	+	+
Resistance to temperature.....	+	?	+	+	+	-	+	?
Electrical resistance.....	?	?	+	+	-	?	?	?
Dielectric constant.....	?	?	?	-	+	?	?	?
Resistance to swelling.....	+	+	+	?	?	-	+	+
Adhesive power.....	?	+	-	?	+	+	-	-
Resistance to cold flow or creep.....	+	?	+	-	+	-	+	+
Resistance to moisture.....	+	+	+	?	?	-	+	+
Resistance to acids.....	?	?	+	+	?	?	+	?
Resistance to alkalis.....	?	?	+	+	?	?	+	?

A plus sign means that the property under consideration increases; a minus sign means that it decreases. A question mark indicates that the effect on the property is not known.

Mainly after

MARK, H., *Ind. Eng. Chem.*, **34**, 1343 (1942).

329. Structural Potentialities of Organic High Polymers. That the covalent bond may be inherently capable of successful competition with the metallic bond for some structural purposes is indicated in Table 3-5. It is often important that a structure be both strong and light, aircraft members affording a notable example. The structural metals are heavy, while organic materials are light, with densities ranging between 1.0 and 1.5. *The specific strength, or strength-weight ratio, of a material is its strength divided by its density and thus takes into account both factors. It affords a comparison of structural materials on an equal weight basis.*

TABLE 3-5. ~~68~~STRENGTH-WEIGHT PROPERTIES OF METALS AND ORGANIC HIGH POLYMERS

Material	Tensile strength, psi s_u	Specific gravity ρ	Strength-weight ratio. Specific tensile strength s_u/ρ
Structural steel (SAE 1020).....	65,000	7.8	8,300
High-tensile stainless steel.....	180,000	7.8	23,000
Dural.....	55,000	2.8	20,000
Wood (aircraft spruce).....	10,000	0.5	20,000
Flax yarn.....	70,000	1.5	47,000
Cotton yarn.....	30,000	1.5	20,000
Nylon yarn.....	50,000	1.1	45,000

The last column of Table 3-5 discloses the fact that at room temperature, pound for pound, flax and nylon yarn are five to six times as strong in tension as ordinary structural steel. The table by no means tells the whole story. At atmospheric temperatures, organic high polymers exhibit much more creep or cold flow than metals, and at elevated temperatures they are so weak that they cannot compete at all. Nevertheless, there are fields of structural applications where they very definitely can outperform metals. The subject is discussed in considerable detail in Chap. 9.

At any rate, in the past our knowledge of structural materials has been entirely too empirical. The requirements of aircraft and high-speed machines have imposed more exacting demands on our knowledge, and the time has come for greater cooperation between the engineer and the physical chemist in the study and development of structural materials. No better meeting ground exists for such concerted effort than the study of high polymers. Cement, mortar, glass, wood, and plastic plywood are all high polymers.

REFERENCES

See Appendix A.

PARTICULAR TOPICS**Plasticization**

SPURLIN, H. M., A. F. MARTIN, and H. G. TENNENT, *J. Polymer Sci.*, **1**, 63 (1946).
Symposium on "Plasticizers," *J. Polymer Sci.*, **2**, 113-198 (1947).

See references accompanying tables and figures of this chapter.

CHAPTER 4

POLYMER FORMATION AND MODIFICATION

400. Mainly because of their special physical properties, the chemical production and manipulation of high polymers involve procedures somewhat different from those applied in making small molecules. To cite just one example, if a B-stage resin is being produced from a polyfunctional set of reactants, conditions must be established that will favor the formation of linear, functional molecules rather than space polymers since, if cross-linkage occurs, the mass will gel, or set, in the reaction vessel. Not only may it be very difficult to remove from the equipment, but also it may be useless for commercial application, for, once cross-linked, it cannot be molded to shape.

CONDENSATION POLYMERIZATIONS

Polar groups such as —OH , —COOH , —NH_2 , —COO— , —CONH— , etc., have very different chemical characteristics. Products such as H_2O , NaCl , HBr , etc., are easy to identify. Consequently, it is a general characteristic of condensation polymerizations that their over-all course is readily established.

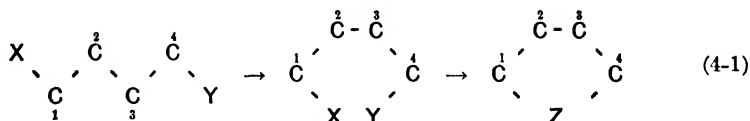
401. Mechanism. Condensation polymerization appears to be a step-wise process and seems to resemble the condensation of analogous small molecules in many respects. Thus, for a polyesterification the activation energy, heat of reaction, and effective catalysts are much the same as those for the esterification of similar small molecules. Although the literature on condensation polymerizations is voluminous, surprisingly few studies have been made to establish the details of the reaction mechanisms. The effort has been directed mainly to determining the conditions under which final products of desired properties may be made rather than to speculating on the mechanisms of the reactions.

402. Effect of Structure of Monomers. In Secs. 109 *ff.* the relations between functionality and polymerization were presented, and Carothers' experiments on condensation polymerization were described. From his brilliant, definitive investigations it is clear that although temperature, concentration, etc., exert their influences as usual, the strongest determinant of the course followed by a polycondensation is the architecture of the reacting monomers. Thus, if the architecture is such that 5- or

6-membered rings *can* form by intramolecular reaction, they *do* form and cyclic monomers rather than high polymers are obtained as the product.

The overwhelming majority of all cyclic compounds that have been isolated and identified prove to have 5- or 6-membered rings. From this one may deduce that such structures are more stable than larger rings, easier to form, or both. It happens that 9-, 10-, and even 16- and 17-membered ring compounds have been prepared. It is true that their preparation is usually difficult, but it is not true that they are unstable. Once obtained, they may be distilled without decomposition and in other respects prove to be just as stable as pentagonal or hexagonal structures, if not more so.

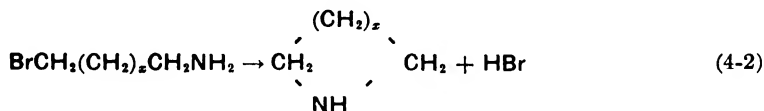
The frequent and ready formation of 5- and 6-membered rings by the intramolecular reaction of two functional groups on the same molecule is simply and satisfactorily explained as follows: In an aliphatic chain, for example, not only is the normal bond angle between the carbon atoms about 110 deg (Table 2-2), but there is rotation around each single bond, so that in solution, or in the liquid state, the chains may whip about into a great many different positions. Suppose a functional group —X is on carbon 1 and another functional group —Y is on carbon 4. Since the normal bond angles, which are close in magnitude to the internal angles of a hexagon or pentagon, are maintained during rotation, it follows from geometry that —X and —Y will collide frequently and permit many opportunities for reaction.



Suppose, however, that —X were on carbon 1 and —Y were on carbon 7 or 10. The probability of intramolecular collision and cyclization would be greatly reduced. An obvious implication is that a huge, cyclic structure for a high polymer such as postulated in reaction (1-10), page 10, is highly improbable.

Now in a liquid melt or solution of a bifunctional compound there is always the probability of *intermolecular* reaction. In other words, the *intra-* and *intermolecular* reactions are always competitive. Consequently, a second implication is that the formation of high polymers rather than cyclic monomers in this type of reaction depends upon the absence of a tendency toward ring closure in the early stages of reaction and that the probability of ring closure will diminish as the length of the chain (distance between functional groups) increases. These concepts are substantiated by the kinetic studies on bromoparaffin amines shown

in Table 4-1. The ring-forming and polymerization reactions involved in these studies are shown in Eqs. (4-2) and (4-3).



The structure of a bifunctional monomer manifests its importance in still other ways. For example, compounds such as *p*-NH₂C₆H₄(CH₂Cl

TABLE 4-1. POLYMERIZATION VS. CYCLIZATION

Bromoalkyl amine	k_1	k_2	k_3
Br(CH ₂) ₆ NH ₂	120	Very small	Very small
Br(CH ₂) ₈ NH ₂	2	Very small	Very small
Br(CH ₂) ₁₁ NH ₂	2.5×10^{-2}	0.6	12
Br(CH ₂) ₁₃ NH ₂	4.2×10^{-2}	1.2	6
Br(CH ₂) ₁₄ NH ₂	4.8×10^{-2}	1.2	5.5
Br(CH ₂) ₁₆ NH ₂	9.0×10^{-2}	1.2	3.0

k_1 is rate constant for the ring formation involving only the monomer (reaction of first order).

k_2 is rate constant for cyclic dimerization (reaction of second order).

k_3 is rate constant for chain formation (reaction of second order).

SALOMON, G., *Trans. Faraday Soc.*, **32**, 153 (1936).

show no tendency whatever to form cyclic monomers even though theoretically the result of intramolecular condensation is a 6-membered ring. The benzene ring itself is a rigid, planar structure, and it is simply a steric impossibility for the two functional groups to reach across it. Again, if two of the atoms of a chain are adjacent atoms of a benzene ring, their position with respect to one another is fixed. Free rotation does not take place around benzene bonds or double bonds, so that the chances for intramolecular reaction are not the same as in an aliphatic chain of identical length. Thus, NH₂(CH₂)₆Cl reacts intramolecularly to form a 7-membered ring only slightly, whereas, with *o*-NH₂C₆H₄(CH₂)₄Cl, closure to form a 7-membered ring is quantitative. In passing, it is interesting to note that the majority of known 7- and 8-membered ring compounds have at least two of their ring atoms joined by bonds about which rotation does not take place.

403. Effects of Temperature, Catalyst, and Solvent. In general, the effects of temperature, catalyst, and solvent upon polycondensations are very similar to those on low-molecular-weight reactions between monofunctional reactants of analogous chemical composition.

Table 1-2 reveals that, regardless of the particular alcohol and acid

used by Carothers in his earlier syntheses of linear polyesters, the average molecular weight of the final product was always of the same order. The total range of values was 2,300 to 5,000. The polymers "died" at this size instead of growing to the astronomical lengths theoretically possible. Carothers himself, and many others after him, thought that this could be explained as follows: as the D.P. increases, the viscosity of the mass increases; this introduces two deterrents to further reaction, a restricted mobility of the reacting molecules and a mass so viscous that the water of condensation cannot escape. The two implications were that the functional groups on large molecules were less reactive than those on the original monomers and that unexpelled water established equilibrium in reaction (1-12), page 12.

Subsequently, however, Flory demonstrated that functional groups on large molecules are just as reactive as those on monomers, and that under the conditions of Carothers' experiments neither the viscosity of the medium nor the rigorousness of expulsion of the water of condensation was the controlling factor of molecular growth, and that Carothers' early polyester products had low molecular weights because equilibrium had *not* been reached. In other words, the higher molecular weights of Carothers' superpolymers (Sec. 237) are traceable to lengthening of the reaction time rather than to displacement of the equilibrium point. Flory is, of course, careful to point out that, when the molecular weight and the viscosity become *extremely high*, the reaction mass is immobilized to the extent that diffusion of the reactants may actually become the rate-controlling step.

High reaction temperatures may cause branching through various mechanisms such as orthoesterification in the case of polyesters.

Condensation polymerizations are often conducted in solution. There are solvent effects as usual. As polymers grow, they tend to drop out of solution as an insoluble phase. This may serve as a means of fractionation. Distillation *in vacuo* or scrubbing with a stream of inert gas may be employed to remove solvent, unreacted monomers, and other low-molecular-weight materials when the reaction has been carried to the desired point. They also protect the reactants from oxidation, a matter of prime importance in the preparation of polyesters and nylons.

If a monomer is of such character that it can condense either intra- or intermolecularly, extensive dilution with a solvent reduces the number of intermolecular collisions and hence favors intramolecular ring closure.

404. Effect of Monomer Concentrations. If two bifunctional reactants such as those of Eq. (1-12) are mixed in equimolar proportions, the reaction can theoretically proceed indefinitely and a high average molecular weight can be attained in practice. But if a considerable excess of

one reactant is employed, the degree of polymerization is decreased. In the limiting ratio of 2 moles of one reactant to one of the other, the product is not a high polymer at all. *Blocking* occurs, and the main yield is a "trimer."



As explained in Sec. 114, in a *polyfunctional* system, whether one obtains linear or space polymers depends upon the relative amounts of the different types of monomers that react. Obviously, then, in a tri-bifunctional system a larger than equimolar proportion of the bifunctional reactant will favor cross-linkage and gelation, while a less than equimolar amount will tend to limit reaction to the bi-bifunctional type and favor the formation of linear functional molecules. Catalysis and temperature control also aid in directing the course of the reaction. Nevertheless, in preparing a mutable polymer there is always danger of premature cross-linkage, which would render it unfit as a binder. Consequently, very careful control must be maintained during manufacture of such resins.

405. Investigational Difficulties Encountered in Space-polymerized Systems. Some natural space polymers such as diamond, mica, asbestos, and other silicates exhibit well-developed crystallinity (Fig. 5-27), and analysis of their x-ray diffraction patterns makes possible the determination of their molecular structure. On the other hand, no synthetic space polymer has yet been prepared that possesses a well-defined x-ray spot pattern. The x-ray photographs show broad halos characteristic of the disordered state (Fig. 5-33). Furthermore, when cross-linkage takes place, the product becomes insoluble and infusible; unreacted monomers, solvent, side products, and impurities are trapped and absorbed in the gel so that stoichiometric analysis is fruitless; the material has no well-defined physical constants. For these reasons, kinetic studies of the cross-linked stages of a polyfunctional reaction are extremely difficult to conduct. At the current writing, the mechanisms of cross-linking reactions and the molecular structures and chemical compositions of condensation mutaplasts such as phenol-aldehyde, urea-aldehyde, and glycerol-phthalic acid resins are more a matter of inference than rigorous experimental proof.

406. Carothers' Equation. Carothers developed an equation relating functionality and degree of polymerization to extent of reaction and gel formation. This simple equation correlates much of the previous discussion. From it one may predict the conditions under which gelation will probably occur, the effects of blocking agents, and the completeness of reaction required to attain any desired degree of polymerization.

Let f = degree of functionality, *i.e.*, the *average* number of functional groups per monomer (when two reactants are used, f is calculated for equivalent amounts)

N_0 = total number of monomer molecules initially present

N = total number of molecules present after reaction has occurred

Then

N_0f = total number of functions present at start of reaction

$2(N_0 - N)$ = number of functions lost, since two functions react in the formation of one bond

$\frac{2(N_0 - N)}{N_0f}$ = fraction of functions lost = p = extent of reaction

Obviously,

$$\frac{N_0}{N} = \text{average degree of polymerization} = n$$

Hence,

$$p = \frac{2}{f} - \frac{2}{nf} \quad (4-5a)$$

When n is infinite or very large, the second term disappears and

$$p = \frac{2}{f} \quad (n \rightarrow \infty) \quad (4-5b)$$

Equation (4-5b) tells the extent of reaction necessary to reach infinite molecular weight and presumably infinite "viscosity," that is, gelation.

If only bifunctional reactants are present, these equations reduce to

$$p = 1 - \frac{1}{n} \quad (4-6a)$$

and

$$p = 1 \quad (n \rightarrow \infty) \quad (4-6b)$$

Equation (4-6b) states that, to reach an average D.P. of only 10, the reaction must attain 90 per cent completion, whereas to reach an average D.P. of 100, which, incidentally, is not very high, the extent of reaction must be 99 per cent. The importance of complete reaction [Eq. (1-12)] if high D.P.'s are to be effected is now evident.

Equation (4-6b) states that infinite molecular weight in a bifunctional system requires complete reaction. In actual practice, complete reaction cannot be effected, and it is a matter of fact that, no matter how far a

bifunctional condensation is carried in ordinary practice, the product is usually still fusible and soluble—irreversible gelation does not occur.

Let us now turn to a typical polyfunctional system. If 2 moles of glycerol and 3 moles of succinic acid, $\text{HOOC}(\text{CH}_2)_2\text{COOH}$, are heated and permitted to react at random, the viscosity of the mixture changes only slowly at first and then suddenly rises enormously. The sudden rise is accompanied by gelation, and analysis shows that much of the acid is left still unreacted after the gel has formed. In this system, the 2 molecules of glycerol contribute 2×3 functions, and the 3 succinic acid molecules contribute 3×2 functions. Since there are 5 reaction molecules in all, $f = 12/5 = 2.4$ and, from Eq. (4-5a),

$$p = \frac{2}{2.4} - \frac{2}{2.4n}$$

Then, at $n = \infty$,

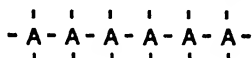
$$p = \frac{2}{2.4} = 0.83$$

In words, according to Carothers' equation the reaction cannot be carried beyond the point where 83 per cent of the functional groups have reacted without the formation of an insoluble, infusible gel, provided, of course, that the reaction is all intermolecular. Since gelation involves immobilization, unreacted material is bound to be present. Assume now that in this same system it is possible to control conditions in such a manner that all the glycerol molecules could be made to react bifunctionally before any react trifunctionally. This would lead to the formation of polyester *chains* with the loss of only two-thirds of the glycerol functions. One-third of the succinic acid would still remain unreacted. In this postulated extreme, only two-thirds of the functions are lost, or p is 0.67. Since the product of reaction would still be a linear polymer, gelation would presumably be avoided. If, however, any further reaction were to take place, it would of necessity involve cross-linkage between chains. This would be accompanied by gelation since the molecular weight would rise to infinity upon the introduction of only a few cross links.

In summary, for the above case Carothers' function indicates 67 per cent as the minimum extent of reaction compatible with gelation and 83 per cent as the maximum. Many experimental values found by various investigators for the extent of reaction at gelation lie between 75 and 80 per cent.

The suddenness of gelation, *i.e.*, the appearance of a sharp break in the viscosity curve with an almost vertical rise, is an important and frequently observed phenomenon. For the sake of simplicity, let us

consider tetrafunctional monomers which first react bifunctionally to form linear chains in which each mer still possesses two functional groups.



Assume further that all the molecules have polymerized to a D.P. of 100. We could reasonably expect that no gelation has taken place and that the mass is soluble and fusible. Since $f = 4$ and $n = 100$, $p = 49.5$ per cent. If further reaction occurs, it must involve cross-linkage; and, with the loss of only two additional functional groups from each chain, all the chains could presumably be joined into one supermolecule. This would involve an extra reaction of only 1 per cent. In other words, at the critical value $p = 49.5$ per cent, the average molecular weight will change abruptly from a moderate figure to infinity. Gelation will result, and further reaction will occur with difficulty.

One more point is of both theoretical and practical importance. This is the *blocking effect* produced by a slight excess of one of the reacting monomers or the introduction of a relatively small amount of a monofunctional reactant. In such case, even at complete reaction, n is finite, and the degree of reaction is limited to some lower value represented by

$$p = \frac{2}{f} - \frac{2N}{N_0f} \quad (4-7)$$

This principle is of importance for control of polymer molecular weight and of viscosity. Thus, such stabilizers are used in the manufacture of nylon to eliminate the possibility of slow, progressive "afterpolymerization," which causes a troublesome change in viscosity during spinning. Such change in viscosity results in nonuniformity in both fiber diameter and strength. This principle is illustrated by the following data on the polyamide prepared from pentamethylenediamine and sebacic acid. The viscosity of molten polymer stabilized with 2.5 per cent excess sebacic acid remained essentially constant at 218 C, increasing to 515 poises from 480 poises in 5.5 hr, whereas the melt viscosity of unstabilized polymer increased nearly fivefold, *i.e.*, to 2,290 poises from 490 poises in 2 hr. Monofunctional blocking agents such as acetic acid act similarly. In such bi-bifunctional systems the number of molecules, S , of excess bifunctional component or of monofunctional reactant will exactly equal the number of polymer molecules, N , after complete condensation. The limiting D.P. is given by N_0/S . The limiting magnitude of extent of reaction is

$$p = 1 - \frac{S}{N_0} \quad (4-8)$$

407. Size Distribution in Linear Condensation Polymers. From statistical theory, Flory has developed a more detailed exposition of polymerization reactions than that embraced by Carothers' equation. This exposition has been of inestimable value in the development of high-polymer theory.

It has already been stated that the molecules of a polymer mass are not all of the same size. By the statistical approach, Flory has developed the equation for the probable size distribution in linear polymers formed via bifunctional and bi-bifunctional condensations involving one single

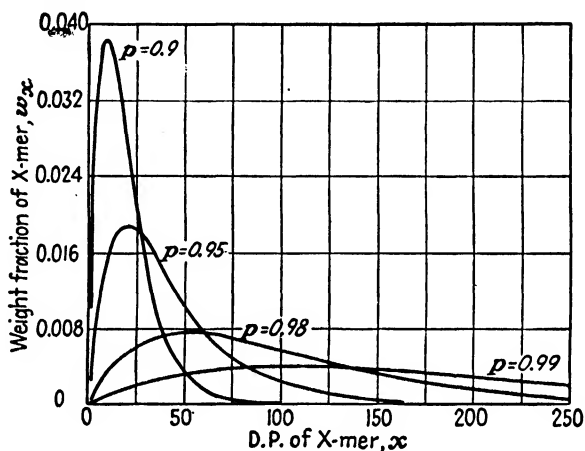


FIG. 4-1. Distribution of linear condensation polymers for large extents of reaction. One rectangle = 0.2 weight fraction. [P. J. Flory, *J. Am. Chem. Soc.*, **58**, 1877 (1936).]

type of elementary reaction, *e.g.*, esterification or amidation. An important limiting assumption is that the reactivity of a functional group is independent of the size of the molecule to which it is attached. Condensation polymerizations generally adhere to this condition.

If x is the number of mers in an individual chain molecule, Flory has shown that, when equivalent amounts of the reacting functions are present,

$$w_x = xp^{x-1}(1-p)^2 \quad (4-9)$$

where w_x is the weight fraction of x -mer; that is, Eq. (4-9) gives the weight fraction of each size of polymer present at any given extent of reaction, p . The size distributions of polymers for several large extents of reaction are shown in Fig. 4-1. This function has been experimentally confirmed both directly and by its successful application to the treatment of other problems.¹

¹ It should be noted that many polymeric products do not possess the size distribution called for by theory owing to fractionations which have occurred either

In Fig. 4-2, w_x is plotted against p for several values of x . The extent of reaction necessary to give maximum yield of a particular x -mer may be calculated from the simple but very useful relation

$$p_x = \frac{x-1}{x+1} \quad (4-10)$$

It so happens that, although the size-distribution curves (Fig. 4-1) are far from symmetrical, the x -mer present in greatest weight fraction is the one for which $x = n$, the average degree of polymerization given by Eq. (4-6a). This relation is only approximate.

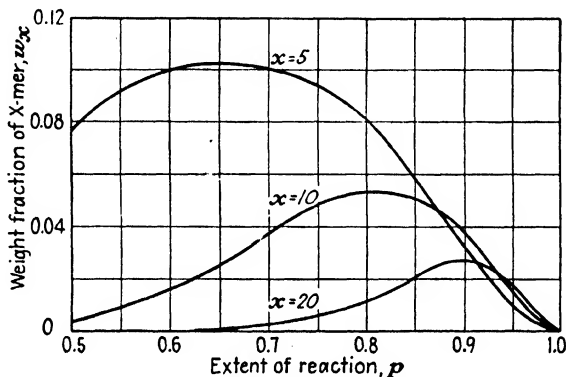


FIG. 4-2. Concentration of particular x -mers as function of extent of reaction. [P. J. Flory, *J. Am. Chem. Soc.*, **58**, 1877 (1936).]

Flory also showed that, for the same reactions under the same limiting assumptions,

$$N_x = p^{x-1}(1-p) \quad (4-11)$$

where N_x is the mole fraction of x -mer present. From this equation it follows that at the conclusion of a polymerization reaction there are more monomers present than any other sized molecule (Fig. 4-3). The weight fraction of monomer present may, however, be very small [Eq. (4-9)].

Furthermore, Flory showed that

$$\frac{\bar{M}_w}{\bar{M}_n} = 1 + p \quad (4-12)$$

that is, as the reaction approaches completion, the weight-average molecular weight approaches twice the number-average.

408. Condensation Space Polymers. It is common experience that in a polyfunctional system gelation takes place long before all the reactants have reacted. This is often deliberately or coincidentally with their preparation, *e.g.*, loss of unreacted monomer via distillation, fractional precipitation of larger, less soluble molecules, etc.

stants are bound together. It is a usual characteristic of such systems that there is a sharply defined gel point at which there is a sudden tremendous increase in viscosity and just as sudden an appearance of insoluble product. However, even after the gel point has been passed, large weight fractions of the product are still soluble.

In order to follow Flory's statistical approach to the analysis of such systems it is necessary to establish certain new terms and definitions.

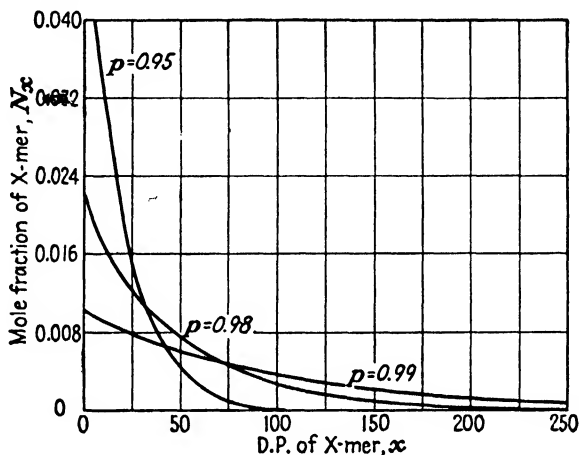



FIG. 4-3. Distribution of linear condensation polymers for large extents of reaction. One rectangle = 0.2 mole fraction. [P. J. Flory, *J. Am. Chem. Soc.*, **58**, 1877 (1936).]

A bifunctional monomer, or "unit," containing two functional groups of type A will be represented by A—A; a trifunctional unit by A—;

etc. It will be recalled that, in order to attain space polymerization, one reactant must possess a functionality of 3 or more so that molecular growth may take place spatially. A monomer, or unit, possessing such a degree of functionality will be called a *branch unit*. Thus in the system glycerol-succinic acid, the glycerol molecules are the branch units. That portion of a polymeric molecule lying between two branch units or between a branch unit and an unreacted terminal group will be called a *chain section*.¹ The chain sections may vary in length, but this is not important at this juncture. A point in the molecule from which three or more chain sections emanate will be known as a *branch point*.

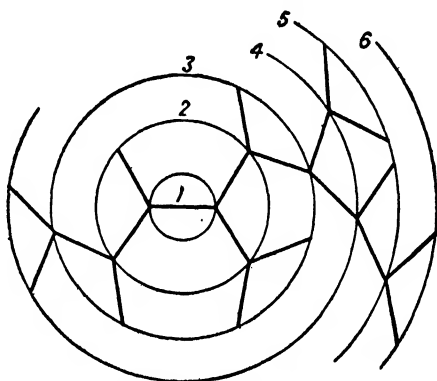
The primary assumption for valid statistical treatment is that during polymerization the probability that any particular functional group has reacted is an independent probability uninfluenced by the number and

¹ Flory uses the term *chain*, but the authors have found this confusing to students.

configuration of other groups in the molecule to which this functional group is attached. Intramolecular reaction will be assumed to be totally absent, an assumption that prevents the results from being exact.

409. Criteria for Incipient Formation of Infinite Networks. Consider a polyfunctional system containing trifunctional branch units $A \begin{smallmatrix} \nearrow A \\ \searrow A \end{smallmatrix}$

reacting with bifunctional molecules $B-B$. Assume that a chain section has been selected at random in the polymer structure and lies within the first circle of Fig. 4-4. The immediate problem is to determine the probability that this chain section is part of an infinite network, when this probability will be greater than zero, and what the fate of the ends of this particular chain section will be. In Fig. 4-4, this chain section gives rise to two branch points, one at each end. The four new chain sections lead to three new branch points (on circle 2) and one terminal group. The resulting six new chain sections lead to two new branch points and four terminal chain sections on circle 3, etc. The molecular network built around the particular chain section of Fig. 4-4 could be designated by 2, 3, 2, 2, 1, 0, where the figures indicate the number of branch points found on each successive circle.



2,3,2,2,1,0 molecule

FIG. 4-4. Schematic representation of a trifunctionally branched space polymer. [P. J. Flory, *J. Am. Chem. Soc.*, **63**, 3083, 3091, 3096 (1941).]

Assume for the moment that there exists a certain probability α that any given functional group of a branch unit leads via bifunctional units to another branch unit rather than to a terminal group. Obviously α will depend on the ratios of the reactants as well as the extent of reaction; that is, α depends on the relative concentration of trifunctional branch

unit $A \begin{smallmatrix} \nearrow A \\ \searrow A \end{smallmatrix}$, the fraction of A groups which have reacted and the fraction

of B groups already reacted. The probability of the other alternative, *i.e.*, that the functional group of the branch unit will lead to an unreacted terminal group, is $1 - \alpha$. It can be shown statistically that, if $\alpha < \frac{1}{2}$, indefinite expansion of the network is impossible since a given chain section has less than an even chance of producing two new ones so that

network propagation eventually ceases. On the other hand, if $\alpha > \frac{1}{2}$, branching of successive chain sections may continue the network indefinitely, leading to molecules of "infinite" size. Hence, in a polyfunctional system containing trifunctional branch units, $\alpha = \frac{1}{2}$ represents the critical condition for incipient formation of infinite structures. However, all the material will not yet be combined into infinite molecules when $\alpha > \frac{1}{2}$. So long as $\alpha < 1$, finite termination of a network is possible. *Consequently, when $1 > \alpha > \frac{1}{2}$, finite molecules will coexist with "infinite" molecules.*

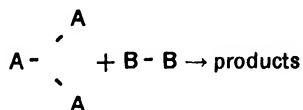
It can be similarly demonstrated that when the branch units are tetrafunctional, e.g., as in pentaerythritol, $C(CH_2OH)_4$, the critical value of α is $\frac{1}{3}$. In general,

$$\alpha_c = \frac{1}{f_b - 1} \quad (4-13)$$

where α_c is the critical value for the formation of infinite molecules and f_b is the functionality (≥ 3) of the branch units interpolymerized at random. (Note the difference between this f_b and the f of Carothers' functions.)

Expressed in terms of direct practical application, Eq. (4-13) states that the introduction of branch units of successively higher functionality into a polyfunctional system of reactants progressively increases the probabilities of three-dimensional growth and gelation, i.e., the conversion of a thermosetting system to its thermoset form is rendered progressively easier to accomplish. The commercial use of monomers of high functionality is expanding at the current writing, as in the case of pentaerythritol (tetrafunctional) and mannitol (hexafunctional) in the manufacture of polyesters, and melamine (potentially hexafunctional) in the manufacture of melamine-aldehyde resins.

410. Calculation of α Values. *Case 1.* Consider a polyfunctional system containing two different kinds of functional group, A and B (e.g., COOH and OH), in the following mixture:



Assume that all groups of the same kind are equally reactive.

The probability P_A that any particular A group has undergone reaction equals the fraction of total A's that have reacted. Similarly, P_B is the fraction of B's reacted; and if r is the ratio of all A to all B groups, then $P_B = rP_A$. This follows because the number of reacted A's equals the

number of reacted B's. Then

$$\alpha = rP_A^2 = \frac{P_B^2}{r} \quad (4-14a)$$

In the special case where the A and B groups are present in equivalent quantities,

$$P_A = P_B = P$$

and

$$\alpha = P^2 \quad (4-14b)$$

From these equations it is evident that the value of α can be determined from a knowledge of the original composition and an analytical-chemical determination of the extent of reaction.

The extent of reaction that yields the critical value, $\alpha = 1/2$, is

$$P_A P_B = 1/2 \quad (4-15)$$

If A groups are present in excess, $r > 1$; and $P_B = 1$ and $P_A = 1/r$ when reaction is complete. If B groups are originally in excess, $r < 1$; and $P_B = r$ and $P_A = 1$ upon completion of reaction. Hence, it follows from Eq. (4-15) that the critical value of α can be reached only when r lies within certain limits, that is, $2 > r > 1/2$. Too great an excess of one kind of functional group or another not only can prevent infinite network propagation but can stop formation of high polymers altogether (Sec. 404).

In glycerol, the secondary alcohol group is less reactive than its two primary alcohol groups. One of the basic assumptions upon which the previous equations were derived is not met, and they do not apply in glycerol-dibasic acid systems. Modified equations then become necessary.

Case 2. For a polyfunctional system of reactants where the branch unit is tetrafunctional and reacts with a bifunctional reactant, equations analogous to those stated under Case 1 may be established. The critical value of α is $1/3$ and is reached when

$$P_A P_B = 1/3 \quad (4-16)$$

Case 3. Consider the limiting case of long chain sections. According to the original definition, α is the probability that a chain section proceeding from a branch unit will end with another branch unit. However, α is not, in general, exactly equal to the probability that a chain which is terminated at one end by an unreacted functional group will lead to a branch unit at the other end. However, for the limiting case of very long chain sections, when both r and P approach unity, the latter probability and α become identical. Also, α approaches the ratio of chain

ends at branches to the total number of chain ends, i.e.,

$$\alpha \cong \frac{f_b \text{ (number of branch units)}}{f_b \text{ (number of branch units)} + \text{(number of unreacted functional groups)}} \quad (4-17)$$

411. Molecular Distribution in Systems Containing Trifunctional Branch Units. A simple diagram will show that, in a system where the branch units are trifunctional, a network or molecule combined by n branch points contains z chain sections, where $z = 2n + 1$. The quantity z will hereafter be known as the *molecular complexity*. (It is important to bear in mind that the chain sections are not of uniform length.) With the probability α defined as previously, the probability that both ends of a chain section selected at random will lead to branch units is $\alpha \times \alpha = \alpha^2$. The probability that there will be a branch at one end and an unreacted terminal group at the other is $\alpha(1 - \alpha)$. This latter quantity will hereafter be designated by the symbol β .

It can be shown statistically that the weight fraction w_z of molecules or networks composed of z chain sections is

$$w_z = (1 + \alpha)^2 \frac{(z + 1)! \beta^{(z-1)/2}}{[(z + 1)/2]! [(z + 3)/2]!} \quad (4-18)$$

where z is restricted to odd integral values. Hence w_n , the weight fraction of molecules containing n branch points, may be expressed in the form

$$w_n = (1 - \alpha)^2 F(\beta, n) \quad (4-19)$$

At the critical point in these systems, $\alpha = 1/2$, and $\beta = 1/4$. The function w_n has three interesting features. First, w_n approaches 0 as n approaches infinity for all values of β from 0 to $1/4$. Second, the series $\sum_{n=0}^{\infty} w_n$ converges for all values of β in the same range. Third, as α [Eq. (4-19)] increases from 0 to $1/2$, β increases from 0 to a maximum of $1/4$ when α is $1/2$; then, as α increases from $1/2$ to 1, β returns from $1/4$ to 0. It follows that, for every value of β (except $1/4$), there will be two values of w_n , one below the critical point, where $\alpha < 1/2$, and another above the critical point, where $\alpha > 1/2$.

The sum of the weight fractions of all molecules of finite size, w_s , and the sum of the weight fractions of all infinite networks, w_o , can be shown to be related as follows:

$$w_s + w_o = 1$$

$$w_s = 1 \quad \text{when } \alpha \leq 1/2 \quad (4-20)$$

$$w_s = \frac{(1 - \alpha)^2}{\alpha^2} \quad \text{when } \alpha > 1/2 \quad (4-21)$$

Also,

$$w_g = 1 - w_s = 0 \quad \text{when } \alpha \leq \frac{1}{2} \quad (4-22)$$

and

$$w_g = 1 - w_s = \frac{2\alpha - 1}{\alpha^2} \quad \text{when } \alpha > \frac{1}{2} \quad (4-23)$$

If N equals the total number of chain sections and Y is the total number of branch points in the mass and no intramolecular reaction occurs, the total number of networks or molecules is

$$N - 2Y = N \left(1 - \frac{4\alpha}{2} \right)$$

Then the number-average number of chain sections per molecule, that is, the *number-average complexity*, is

$$\bar{z}_n = \frac{1}{1 - 4\alpha/2} \quad (4-24)$$

The weight-average number of chain sections per molecule, or *weight-average complexity*, is

$$\bar{z}_w = \sum_{n=0}^{\infty} (2n + 1)w_n \quad (4-25a)$$

When n is large, \bar{z}_w may be shown to be

$$\bar{z}_w = \frac{2(1 - \alpha)}{\alpha \sqrt{\pi}} \sum_{n=0}^{\infty} \frac{(4\beta)^{n+1}}{\sqrt{n+1}} \quad (4-25b)$$

The series in Eq. (4-25b) is convergent for all values of β up to the critical point $\beta = 1/4$. At the critical point, \bar{z}_w reaches infinity. Beyond the critical point, \bar{z}_n and \bar{z}_w for that fraction of the mass composed of molecules of finite size are given by the above equations when α ($> 1/2$) is replaced by $1 - \alpha$. As the polymerization reaction proceeds, not only does the degree of branching α increase, but also the lengths of the chain sections. In other words, the average molecular weights increase more rapidly than the corresponding molecular complexities z . Equations (4-24) and (4-25) do not, therefore, express the exact course of the number-average and weight-average molecular weights. Nevertheless, it can be shown that the ratio $\bar{M}_w/\bar{M}_n \cong \bar{z}_w/\bar{z}_n$. This ratio (Sec. 108) increases with α when $\alpha < 1/2$ and attains infinity at the critical point $\alpha = 1/2$.

In Fig. 4-5, w_g is plotted against α , as are values of \bar{z}_n and \bar{z}_w , and the sharp breaks and discontinuities predicted by statistical theory are shown.

412. Experimental Results. In the light of what has gone before it is natural to postulate that the experimental gel point encountered in a

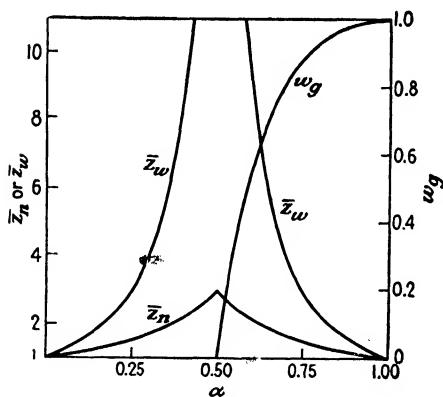


FIG. 4-5. Weight fraction of gel and other properties as functions of α for a space polymer system containing trifunctional branch units. The \bar{z}_n and \bar{z}_w curves beyond $\alpha = 0.5$ refer to the sol fraction only. [P. J. Flory, *J. Am. Chem. Soc.*, **63**, 3091 (1941).]

These yield the value $\alpha_{\text{crit}} = \frac{1}{2}$, confirmed by experimental values of 0.58 to 0.62. It should be recalled that the statistical treatment is based on the assumption that no intramolecular reaction occurs.

polyfunctional system of reactants should correspond with the theoretical critical point for infinite network formation. This has been tested and confirmed in a number of cases covering different types of systems. For example, careful measurements were made on the system tricarballic acid-dicarboxylic acid-glycol, which is more complicated than Case 1 above in that it is of

the type $A-\begin{matrix} \diagup A \\ \diagdown A \end{matrix}$, $A-A$, $B-B$.

Nevertheless, by similar treatment, equations more complicated but of the same general form as those above can be derived.

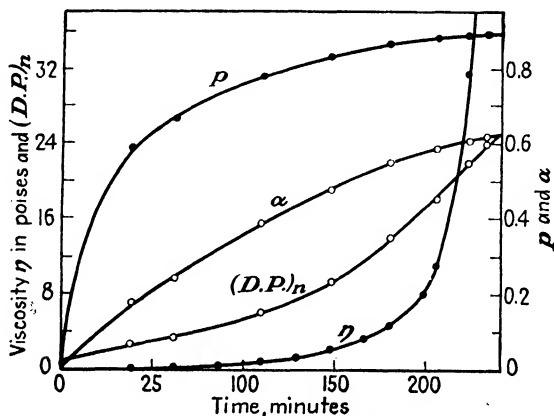


FIG. 4-6. Gelation phenomenon in space polymerization of tricarballic acid-succinic acid-diethylene glycol (109 C, *p*-toluenesulfonic acid catalyst). [P. J. Flory, *J. Am. Chem. Soc.*, **63**, 3083 (1941).]

The results of one experiment are shown in Fig. 4-6. There was no difficulty in locating the experimental gel point from sharp changes in

viscosity and solubility that occurred there. Samples removed prior to gelation were completely soluble in appropriate solvents (*e.g.*, chloroform), whereas samples removed just after gelation contained a definitely insoluble component. The experimental viscosity increased slowly at first, then very rapidly as the gel point was approached.

In a similar experiment involving the polymerization of pentaerythritol, $C(CH_2OH)_4$, with an equivalent amount of adipic acid ($r = 1$), gelation occurred at $p = 0.606$. This corresponds with $\alpha = p^2 = 0.366$ compared with a theoretical $\alpha_{crit} = 0.333$ for tetrafunctional branch units, again on the high side.

From these results it is concluded that α_{obsd} is higher than α_{theo} but close enough to lend support to the hypothesis that gelation in polyfunctional systems is attributable to the formation of infinitely large molecules. If only 2 to 6 per cent (depending on ingredients and their ratios) of the interunit linkages are assumed to be *intramolecular*, perfect agreement with theory is obtained.

413. Discussion. It has been shown that the statistical treatment not only accounts well for the qualitative behaviors of space polymers but permits quantitative treatment. The gel point for the particular system corresponds to the critical value for α that marks the initiation of the propagation of molecules of infinite molecular weight.

So long as $\alpha < 1$, network termination is still possible, which means that above the critical value molecules of finite molecular weight, presumably soluble, coexist with molecules of infinite molecular weight, presumably insoluble. w_s and w_g of Eqs. (4-20) to (4-23) therefore represent weight fractions of sol and gel, respectively. w_s/w_g is the *sol-gel ratio*. In accord with fact, the statistical equations indicate that, below the gel point, $w_s = 1$ and the mass is completely soluble. They further indicate a very sudden appearance of giant molecules, presumably insoluble and present to the extent w_g . This again is in accordance with fact.

The statistical analysis applied to polyfunctional systems containing trifunctional branch units indicates that at the gel point, the number-average molecular weight \bar{M}_n is only three-halves what it would be at the same extent of reaction if the trifunctional units were stoichiometrically replaced with bifunctional units; *i.e.*, at the gel point the trifunctional branch units are responsible for a decrease of only one-third in the total *number* of molecules. By contrast, the size distribution is greatly broadened, and there is a very rapid rise in the weight-average molecular weight \bar{M}_w in the neighborhood of the gel point. The disparity between the two molecular weights reaches a maximum at the critical point where \bar{M}_w reaches infinity. Since viscosity depends on \bar{M}_w , an explanation is

provided for the observed increase in viscosity without limit at the gel point, so characteristic of these systems (Fig. 4-6). It is also evident that determination of the point of incipient gelation affords a method for determining molecular weights in polyfunctional systems.

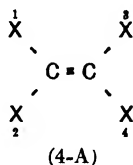
Another interesting characteristic of the size distribution in space-polymerized systems is brought out by Eq. (4-18). For all values of α up to the gel point ($\alpha = 1/2$), a considerable fraction of the material is present in the form of single, individual chain sections ($z = 1$). For α values of 0.15, 0.25, and 0.50, the weight fractions for $z = 1$ are 0.72, 0.56, and 0.25, respectively. At no stage is there any large fraction of material composed of finite molecules of great complexity. Furthermore, from Fig. 4-5 it is seen that after the gel point has been reached and α increases beyond the critical value toward unity, not only does the weight fraction of gel w_g increase, but the molecular complexity and hence the average molecular weight of the sol fraction steadily decrease. In other words, there is a preferential conversion of large complex molecules into infinite networks as α increases. Even at high extents of reaction one should expect to find a soluble extractable fraction of low-molecular-weight material in thermoset and vulcanized products. This is widely confirmed by experiment.

ADDITION POLYMERIZATIONS

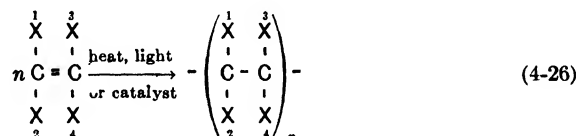
414. Vinyl Polymers. Organic compounds containing unsaturated bonds such as $C=C$, $C\equiv C$, $C=N$, $C\equiv N$, and $C=O$ exhibit a general tendency to polymerize by addition. Indeed, almost any organic compound may be made to yield polymeric products under sufficiently drastic thermal conditions since pyrolysis creates unsaturated structures, which are then capable of addition. However, to be of technical interest an unsaturated compound must be subject to precise control with regard to purity and reaction conditions. Otherwise, polymeric products of uniform quality cannot be manufactured. For various reasons such as cost of production, ease of purification, and reaction control, monomers containing olefinic bonds are the most important for the commercial production of addition polymers.

In olefinic addition polymerizations, strongly polar, readily identifiable functional groups such as $-\text{COOH}$, $-\text{OH}$, and $-\text{NH}_2$ are not involved. Furthermore, bond rearrangements in olefinic structures can take place in more than one way. Important consequences of these two facts are that the course followed by an addition polymerization is (1) more difficult to determine by chemical means and (2) more difficult to control than a condensation polymerization. Undesirable reactions are likely to take place concurrently with a preferred reaction.

Certain guiding principles may be stated relating the molecular structure of an unsaturated monomer to its polymerizability. The most general representation of an olefin is



where the X's may be hydrogens, halogens, alkyl, aryl, ester, or other groups. Many monomers of the above structure polymerize in accordance with the general equation



In this text any reaction of the above type will be called a *vinyl polymerization* whether or not the monomer involved is a vinyl compound, that is, $\text{CH}_2=\text{CH}-\text{X}$, and irrespective of whether or not the polymeric product is generally known as a vinyl polymer. Examples of vinyl polymerization products under this definition are given in Tables 4-2 and 4-3.

TABLE 4-2. POLYMERS FORMED FROM MONOMERS OF TYPE $\text{CH}_2=\text{CH}-\text{X}$

—X	Monomer	Polymer
—H	$\text{CH}_2=\text{CH}_2$ Ethylene	Polyethylene. Exceptional electrical properties
—C ₆ H ₅	$\text{CH}_2=\text{CH}-\text{C}_6\text{H}_5$ Styrene	Polystyrene. Exceptional electrical properties
—Cl	$\text{CH}_2=\text{CH}-\text{Cl}$ Vinyl chloride	Polyvinyl chloride. Binder for nonflammable substitute rubber
—OCOCH ₃	$\text{CH}_2=\text{CH}-\text{OCOCH}_3$ Vinyl acetate	Polyvinyl acetate. Good adhesive. Raw material for derived polymers
—COOR	$\text{CH}_2=\text{CH}-\text{COOR}$ Acrylic ester	Polyacrylates. Exceptional clarity
—OH	$\text{CH}_2=\text{CH}-\text{OH}$ Vinyl alcohol (nonexistent)	Polyvinyl alcohol. Notable resistance to organic solvents

TABLE 4-3. POLYMERS FORMED FROM MONOMERS OF TYPE $\text{CH}_2=\overset{\overset{1}{\text{X}}}{\underset{\underset{2}{\text{X}}}{\text{C}}}$

$\overset{1}{\text{—X}}$	$\overset{2}{\text{—X}}$	Monomer	Polymer
—CH_3	—COOR	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_2=\text{C—COOR} \end{array}$ Methacrylic ester	Polymethacrylates. Exceptional clarity
—Cl	—Cl	$\begin{array}{c} \text{Cl} \\ \\ \text{CH}_2=\text{C—Cl} \end{array}$ Vinylidene chloride	Polyvinylidene chloride. Outstanding resistance to solvents and strong reagents
—CH_3	—CH_3	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_2=\text{C—CH}_3 \end{array}$ Isobutylene	Polyisobutylene. Rubbers of notable resistance to aging and corrosive agents

415. Activation of the Double Bond by Substituents. Ethylene, the simplest possible olefin, is relatively difficult to polymerize to a high level. Pressures of 1,200 atm., temperatures up to 300 C, and a small, carefully controlled amount of oxygen catalyst are the conditions required to produce solid polyethylene of high molecular weight (20,000 or more). This reluctance of ethylene to polymerize may be attributed to a relative lack of activity in the double bond.

It has become evident that the double bond may be made more active and polarizable by (1) substitution which confers polarity on it and (2) substitution which makes it part of a conjugated or potentially conjugated system.

In illustration of the first factor, vinyl chloride and unsymmetrical dichloroethylene (vinylidene chloride) polymerize readily under conditions far less drastic than those for ethylene, presumably by virtue of the polarity conferred on the double bond by the electronegative chlorine atoms, which draw electrons toward them. On the other hand, symmetrical dichloroethylene, $\text{ClCH}=\text{CHCl}$, exhibits no great tendency to polymerize. For that matter, neither does tetrachloroethylene. So far as is generally known, the latter cannot be polymerized at all. This is attributed to steric hindrance around the double bond, the chlorine atom being relatively large. Vinyl bromide and vinyl acetate are other examples of polar activation and ready polymerizability.

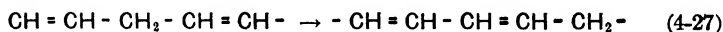
Examples of the second factor, the influence of conjugation or potential conjugation, are butadiene, $\text{CH}_2=\text{CH—CH}=\text{CH}_2$; styrene,

$\text{CH}_2=\text{CH}-\text{C}_6\text{H}_5$; and acrylic esters, $\text{CH}_2=\text{CH}-\text{C}=\text{O}$. All these

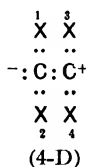
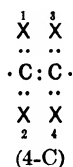
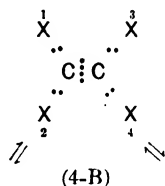


compounds react readily to form high polymers. A conjugated system of double bonds, that is, $\text{C}=\text{C}-\text{C}=\text{C}$, has long been recognized as an arrangement favoring polymerization. Tung oil contains triply conjugated structures, $-\text{CH}=\text{CH}-\text{CH}=\text{CH}-\text{CH}=\text{CH}-$, and polymerizes more readily than linseed oil, which does not contain such systems (Sec. 1403).

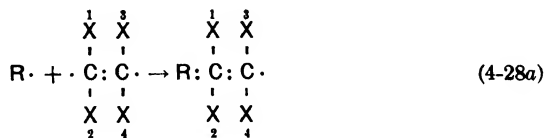
Finally, it should be mentioned that nonconjugated systems of double bonds may sometimes rearrange to conjugated structures under the influence of heat or catalyst.



416. Mechanisms of Vinyl Polymerization. Vinyl polymerization is a chain reaction proceeding by three possible mechanisms, depending upon the type of catalyst used.¹ It is possible to write three resonating structures for vinyl-type compounds with the following electronic representations:



One type of vinyl polymerization starts with structure (4-C). It involves the addition of a free radical.

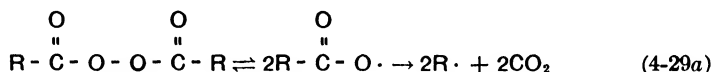


¹ In this and subsequent sections the reader should distinguish between the two uses of the word *chain*, (1) referring to the kinetic mechanism of reaction whereby the energy of activation is passed from one molecule to another and (2) referring to a polymer molecule, as in "chain growth."

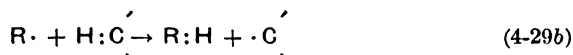
This is the trigger that sets off polymerization. Chain growth then proceeds by the successive, extremely rapid addition of monomers to the above radical to form new ones of continuously larger size.



This step is many times repeated until something happens to deactivate the chain, thus terminating the process. There is usually an induction period during which the free radicals form. These free radicals form from a catalyst or by the action of heat or light on monomers. Peroxides and other highly oxygenated compounds are widely employed as catalysts because they readily form free radicals.



A free radical may also remove a hydrogen atom from a monomer (or polymer) converting the latter into a free radical.

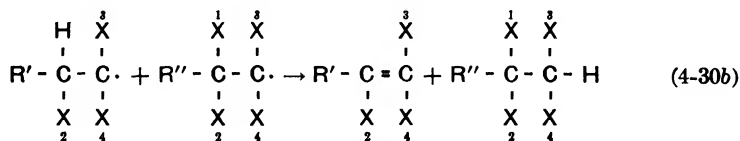


Chain termination takes place by one of the following bimolecular reactions:

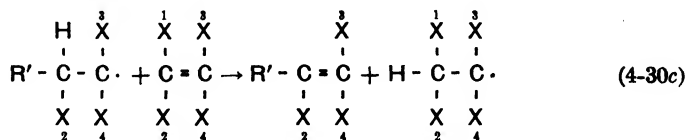
1. Addition of growing chain and free radical, the latter being either a catalyst molecule or another growing chain.



2. Reaction of two growing chains by disproportionation.

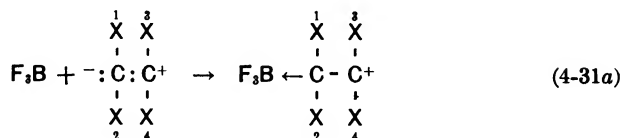


3. Transfer of activation to another molecule, such as polymer, monomer, or impurity, which readily forms a free radical.



A second type of vinyl polymerization starts with structure (4-D). It involves the addition of a catalyst molecule characterized by strong

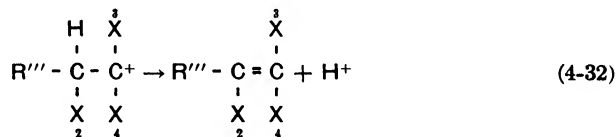
affinity for a pair of electrons. Metal halides such as BF_3 , AlCl_3 , ZnCl_2 , and SnCl_4 are catalysts of this type.



Addition of the catalyst results in the formation of a coordinate bond between catalyst and monomer, and polymerization is initiated by polarization of the double bond of the monomer. Chain growth then proceeds by the successive, extremely rapid addition of monomers to the cationic carbon atom of the above molecule to form new molecules of continuously larger size.

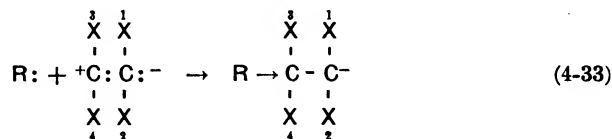


Chain termination in this case takes place through the loss of a proton by the active chain end.



The latter process may also be regarded as transfer of activation because the proton may start a new chain by the same mechanism.

A third possible mechanism of vinyl polymerization also starts with structure (4-D). It involves the addition of an electron-donor catalyst molecule:



Chain growth then proceeds by the successive addition of monomers to the anionic carbon atom. This type of vinyl polymerization is rare.

The various processes involved in vinyl polymerization may be summarized as follows, the symbols M, R, and P signifying monomer, catalyst, and polymer, subscripts signifying the degrees of polymerization, and an asterisk denoting an activated molecule:

1. Chain initiation.



[See Eqs. (4-28a), (4-29a), (4-31a), and (4-33).] Activation energies are of the order of 16 to 30 kcal.

2. Chain propagation.



[See Eqs. (4-28b) and (4-31b).] The time during which a chain remains activated and grows is of the order of 1/1,000 sec. The possible speed of these reactions is indicated by the almost instantaneous conversion of isobutylene at -70°C in the presence of boron trifluoride into very long polymer molecules.

3. Chain termination.



This equation is schematic only; no single summary equation is possible [see Eqs. (4-30a), (4-30b), and (4-32)].

Processes 1, 2, and 3 occur as consecutive reactions. Other mechanisms that may or may not be involved are listed below.

4. Chain transfer.



This equation is also schematic [see Eqs. (4-29b), (4-30c), and (4-32)].

5. Branching. Branching occurs when two growing chains form an inactive polymer and a molecule with two regions of activation, the latter continuing to grow in two directions; or when a growing chain combines with a polymer with continued growth of the reaction product; or when a free radical removes a hydrogen atom from the middle of a chain forming a new region of activation [Eq. (4-29b)].

6. Cross-linkage. Cross-linkage occurs when a growing branch combines with another growing branch or with the main chain of another polymer molecule.

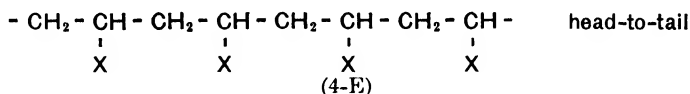
It is evident that addition polymerization differs fundamentally from condensation polymerization. In condensation polymerization the monomer molecules are so constituted that the condensation process is capable of indefinite repetition to build up a polymeric product. The reaction proceeds in a regular, stepwise manner, yielding material of steadily increasing degree of polymerization throughout the course of the reaction. Catalysts are true catalysts in the sense that they are not used up in the course of the reaction.

In addition polymerization, on the other hand, the polymer molecules first formed are essentially the same size as those formed later. (Indeed, often the polymer molecules formed during the early stages of the reaction are of higher molecular weight as well as less branched than those formed at later stages.) That is, the polymer molecules do not grow gradually, but each one grows rapidly to a certain size and is then stabilized. The

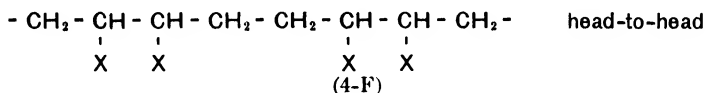
catalysts are reactants in that they combine with the monomers so that the polymer molecules contain fragments from the catalysts as end groups.

417. Vinyl Polymerization and Structure. Vinyl addition polymerizations are markedly affected by the structures of the reactants. Slight changes in structure of monomer or catalyst may change greatly the speed of reaction and properties of the product. For example, some vinyl polymers appear to exhibit little if any tendency toward branching, while in others this tendency is strong.

There is one uniformity, however, in vinyl addition products—the predominant head-to-tail arrangement of the mers.



Another possibility, of course, is a head-to-head arrangement.



The arrangement of the mers can be determined by chemical studies; *e.g.*, a 1,2-dichloride is almost entirely dechlorinated by metallic zinc, whereas in a 1,3-dichloride a predictable proportion of the chlorine atoms is not removed. When polyvinyl chloride is treated with zinc, the amount of chlorine removed agrees with what would be expected from a 1,3 (head-to-tail) arrangement and not from a 1,2 or from a random arrangement. Hence, the arrangement of mers in this polymer is deduced to be head-to-tail. Ultraviolet absorption spectra and x-ray diffraction studies are independent methods for confirming the structures.

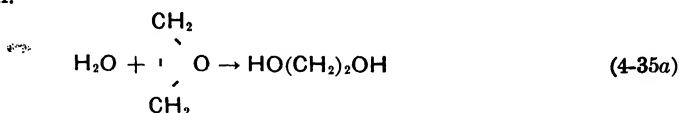
The predominant head-to-tail arrangement follows from the mechanism of vinyl polymerization. The two ends of a nonsymmetrical vinyl monomer molecule will have different tendencies to combine with a catalyst. If the head combines more rapidly, the product of chain initiation is R—head—tail*, and of chain propagation R—(head—tail)_m*. If the tail combines more readily, the product of initiation is R—tail—head*; of propagation, R—(tail—head)_m*. In either case, therefore, the polymer has the head-to-tail arrangement of the mers. (For symmetrical monomers, head-to-head and head-to-tail are synonymous.)

Nevertheless, perfection of arrangement is not present; *e.g.*, careful studies on polyvinyl acetate disclose 1 to 2 per cent of head-to-head arrangement of the mers. This, together with branching, reduces the recurrence symmetry.

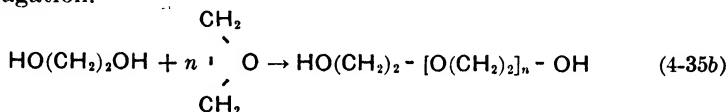
418. Polymerization by Ring Scission. There is another type of polymerization, which has not yet been discussed. It takes place between cyclic monomers, scission of the ring occurring during the reaction. Such polymerization may be classified as addition polymerization, for side products are not split out *between reacting monomers*.

One example of *ring-scission polymerization* is that of olefinic oxides, a reaction in which monomers add to an initiating molecule that has formed by reaction with a trace of catalyst, *e.g.*, water.

Chain initiation.



Chain propagation.



Early efforts to synthesize protein analogues by condensation polymerization of α -amino acids [Eq. (4-49)] or amino acid derivatives had had only meager success, largely owing to the formation of the 6-membered diketopiperazines, $(\text{NHCHRCO})_2$. However, in 1947 it was found that protein analogues with molecular weights in the millions may be made via a ring-scission polymerization starting with cyclic monomers of structure (4-G). The following reactions are involved:

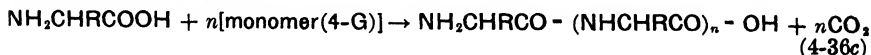
1. Chain initiation.



2. The grouping —NHCOOH is unstable.



3. Chain propagation.



419. Size Distribution in Addition Polymers. The calculation of the polymer size distribution produced in vinyl polymerization is much more complex than for bifunctional condensation (Sec. 407). Various functions have been derived, taking into account the modes of initiation and termination and the occurrence of chain transfer. Under one set of conditions, *e.g.*, a single activation mechanism, termination by disproportionation, and no chain transfer, the size distribution is identical with that for

bifunctional condensations involving one single type of elementary reaction, *i.e.*, Eqs. (4-9) through (4-12) apply. On the other hand, if chain termination takes place through the combination of free radicals instead of by disproportionation, the distribution function is qualitatively similar but not mathematically exactly the same. An example of this latter set of conditions is the uncatalyzed polymerization of styrene for which the experimental and theoretical distribution curves are shown in Fig. 1-2. Chain transfer changes the distribution.

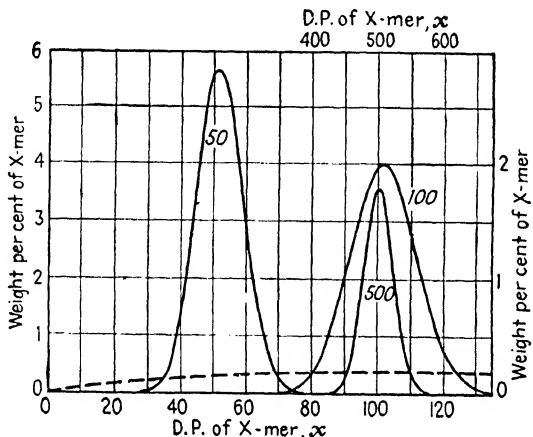


FIG. 4-7. Distribution of ethylene oxide addition polymers for large extents of reaction. Number under each curve is the average number of ethylene oxide molecules added per initiating molecule; hence, average D.P. is this number plus one. The broken curve represents the distribution of a linear condensation polymer at an average D.P. of 101. The scales for the 500 curve are shown upper and right, the scales for the other curves are along the lower and left margins. [*P. J. Flory, J. Am. Chem. Soc.*, **62**, 1561 (1940).]

Ring-scission polymerization produces a size distribution different qualitatively as well as quantitatively from that of condensation polymerization of vinyl addition. In the latter two, growth takes place by the addition of monomers to each other, the addition of monomers to polymers and the addition of polymers to polymers. In the first, on the other hand, growth takes place only by the addition of monomers to polymers, and typical size-distribution curves are shown in Fig. 4-7. They are seen to be quite different from those previously discussed. The far greater homogeneity of these products is reminiscent of that of certain natural polymers.

420. Control of Vinyl (and Diene) Polymerization. From the mechanisms presented in Sec. 416 one would expect the final average degree of polymerization to depend on the ratio of the rate of chain growth to that of chain termination. The conditions extant during reaction affect not only the average D.P. but also the rate at which polymer is produced.

Furthermore, these conditions affect the amount of branching and cross linking. The discussion in this and succeeding sections applies equally well to vinyl and diene polymerizations (Sec. 430).

In the production of vinyl and diene polymers it is almost always desirable to have linear polymers with little or no branching or cross linking. In the early stages of polymerization, initiation and propagation predominate, and the polymer molecules produced are largely linear. However, in the later stages, when the concentrations of monomer and catalyst have been considerably reduced, the undesirable reactions occur more often. Therefore, a widely used method of control is to stop the reaction when about three-quarters completed by adding an inhibitor. The polymer is separated, and the unreacted monomers are recovered.

In the production of diene polymers to be used as rubbers, the employment of chain transfer agents, often called *orientation catalysts*, is common. Examples are the mercaptans, RSH. These help to start new chains, thus decreasing the possibility of branching and cross linking. They also reduce average molecular size, which is not too great a disadvantage in the rubbers, for the subsequent vulcanization builds up the molecule.

421. Effects of Temperature, Catalyst, and Solvent. Several useful generalizations have been established. For a given system,

1. The average molecular weight of the product rises with the percentage of monomer that has undergone polymerization [Eq. (4-9) and Fig. 4-1, page 106].

2. Rise in temperature and catalyst concentration increase the rate of polymer production but reduce the ultimate average molecular weight (Tables 4-4 and 4-5).

TABLE 4-4. EFFECT OF TEMPERATURE AND CATALYST CONCENTRATION ON RATE OF PRODUCTION OF METHYL METHACRYLATE POLYMER
(100 ml of methyl methacrylate monomer in 450 ml of methanol and 450 ml of water heated with benzoyl peroxide catalyst)

Temperature, deg C	With 0.0% catalyst		With 0.1% catalyst		With 0.5% catalyst		With 1.0% catalyst	
	Induction period, hr	Time to reach 95% polymer- ized, hr	Induction period	95% polymer- ized	Induction period	95% polymer- ized	Induction period	95% polymer- ized
65	50	70	4	10	1	4	0.5	2.5
80	0.6	3	0.2	1	0.1	0.5	0.1	0.3

TABLE 4-5. EFFECT OF TEMPERATURE AND CATALYST CONCENTRATION ON DEGREE OF POLYMERIZATION OF METHYL METHACRYLATE (Monomer, solvents, and catalyst as in Table 4-4)

Temperature, deg C	% catalyst			
	0.0	0.1	0.5	1.0
	Molecular weight in thousands			
65	166	140	130	112
80	112	106	78	72
100	110	94	74	54

STRAIN, D. E., *Ind. Eng. Chem.*, **30**, 345 (1938).

3. Dilution with an indifferent solvent lowers the final average molecular weight, and this solvent effect varies considerably from one solvent to the next (Table 4-6).

TABLE 4-6. EFFECT OF SOLVENTS ON POLYMERIZATION OF METHYL METHACRYLATE (Temperature, 65 C. No polymerization catalyst present)

Effect of changing solvent concentration. Monomer dissolved in 95% ethanol			Effect of different solvents. 20% monomer in 80% by volume of solvent in all cases		
% by volume of solvent	Induction period, hr	Final M.W., thousands	Solvent	% yield of polymer in 225 hr	M.W. of polymer, thousands
50	96	90	Dioxane	98	35
70	140	77	Butyl acetate	86	41
80	170	75	Methoxyethanol	97	46
			Ethylene chloride	63	54
			Acetone	73	75
			95% ethanol	75	75

STRAIN, D. E., *Ind. Eng. Chem.*, **30**, 345 (1938).

In industrial practice most vinyl polymerizations are conducted at temperatures between 30 and 150 C, depending on the particular monomer, the reaction medium, and the type of product desired. However, polymerization with metal halide catalysts may be carried out at temperatures as low as -100 C, as in production of polyisobutylene. Most vinyl polymers break down at temperatures above 250 C, and in some instances monomer is recoverable in large percentages.

Unsaturated monomers must be kept in a cool, dark container away from air; otherwise, polymerization will take place during storage.

Furthermore, in industrial practice it is usually necessary to add an inhibitor. Aromatic amines and phenols, especially quinoid compounds such as hydroquinone, exert a strong action and are used with both olefinic and diene monomers. It is interesting to note that these inhibitors are the same types added to cracked gasolines to prevent "gum" formation, which is an addition polymerization. It has been shown that hydroquinone combines with peroxides, one molecule of peroxide being destroyed for each molecule of hydroquinone that disappears. It is probable that all effective inhibitors for chain reactions act similarly by destroying the initiating free radical or other catalyst.

Inhibitors may be of two kinds, those which are effective at both storage and polymerization conditions and those which are active at storage conditions but lose their effectiveness at the temperature and other conditions prevailing during polymerization. Those of the second type are preferable in that they need not be removed before polymerization is conducted. However, such compounds are not always available. Inhibitors of the first type are removed by washing or distillation. It is in some cases likewise essential or desirable to remove catalysts from the product after polymerization has been completed.

Many vinyl and diene monomers are low-boiling liquids. Since in most instances gas-phase polymerization has not proved successful, many of the reactions are run under pressure, the pressure being sufficiently high to keep the monomers in the liquid state.

422. Effects of State of Dispersion. Although numerous polymerization procedures are described in the literature, those most used are the following:

1. Bulk polymerization. The monomers are polymerized in the absence of solvent or diluent. This is also termed *mass polymerization*.

2. Solution polymerization. The monomers are dissolved in a solvent and polymerized.

3. Emulsion polymerization. The monomers are emulsified in a nonsolvent, the dispersed droplets being of the order of 10^{-4} cm in diameter.

4. Suspension polymerization. The monomers are suspended or dispersed in a nonsolvent without the aid of surface-active agents, the dispersed drops being of the order of 0.05 to 0.5 cm in diameter. This is also termed *pearl polymerization*.

Almost any vinyl or diene polymer may be produced by all four techniques, but numerous theoretical and practical reasons dictate the use of one method in preference to the others.

423. Bulk Polymerization. Polymerization reactions are generally strongly exothermic, the heats of reaction for vinyl polymerizations

ranging from 20 to 30 kcal per g mole. Furthermore, as polymerization proceeds, the viscosity rises and heat transfer becomes increasingly difficult. For these reasons, bulk polymerization may be disadvantageous. There may be temperature gradients and local superheating, which result in poor control over size distribution, average molecular weight, and color of the product. To overcome these factors, bulk polymerization must sometimes be conducted in small containers, the ambient temperature being lowered as the reaction proceeds. In other cases, the temperature and rate of polymerization must be held low throughout in order to obtain products of high average molecular weight and superior uniformity and color (Sec. 839). Another disadvantage of bulk polymerization is that catalyst and unreacted monomer are removed with difficulty, if at all. On the other hand, advantages that may accompany this method are rapid production, freedom from retained solvent (or nonsolvent), and no necessity for removing solvent (or nonsolvent).

424. Solution Polymerization. Polymerization in solution mitigates the problems of heat transfer and temperature control. Often the reaction is conducted at the reflux temperature of the solvent. This serves the double purpose of ensuring constant temperature and dissipation of the heat of reaction in evaporating the solvent. If the polymer and monomer are both soluble in the solvent, the polymer is recovered by evaporating the solvent and unreacted monomer or by throwing it down by the addition of a nonsolvent. In other cases, the polymer is insoluble and precipitates as formed. Disadvantages accompanying the method are that solvents retard the reaction and furthermore are almost impossible to remove completely. Retained solvent may impair the properties of the product. The effect of solvents in limiting the final degree of polymerization (Table 4-6) may be either an advantage or disadvantage, depending on the molecular size desired in the final product.

425. Emulsion Polymerization. Emulsion polymerization combines the advantages of the two methods previously described, *viz.*, ease of temperature control, rapid production of polymer, and high average molecular weights. The method is widely applicable to vinyl compounds and has been still more important in the preparation of synthetic (diene) rubbers, where its introduction may truly be said to have effected a major advance in the art. In this method the monomers are dispersed as fine droplets in a large amount of nonsolvent, usually water. Common soaps or special emulsifying agents are usually required. Protective agents such as casein, gelatin, gums, or dextrans are sometimes necessary to stabilize the emulsion. The water is available for absorbing the heat of reaction; and since the dispersed droplets are small, heat transfer is rapid. Control over the reaction is therefore notably improved. Fur-

thermore, the speed of polymer production is often greatly increased. For example, chloroprene standing in bulk at room temperature requires about 10 days to polymerize, whereas, emulsified in a soap solution, polymerization is complete within a few hours at the same temperature. Another advantage of the method is that water-soluble catalysts may be used. They can act at the droplet interface. Indeed, if necessary, both water-soluble and organosoluble catalysts may be utilized simultaneously.

When an emulsion polymerization is complete, the polymerized product is still dispersed as an emulsion or latex. In numerous instances, notably for adhesive, surface-coating, and textile-finishing applications, the product ~~may~~ be sold and used in this form. In other cases, however, the product must be recovered in bulk by breaking the emulsion with electrolytes or solvents, followed by washing and drying. A disadvantage of the method is that impurities (emulsifying, stabilizing, and other agents—Table 13-3, page 554) left in the product may damage electrical and other properties.

426. Suspension Polymerization. Suspension polymerization, of more recent introduction, was developed with an eye toward eliminating the disadvantage of emulsion polymerization while essentially preserving its advantages. The principle is to add no emulsifying agent but to keep relatively large drops of the monomer dispersed in the nonsolvent by mechanical agitation. As polymerization proceeds, the dispersed drops increase in viscosity and reach a sticky stage. If the proper measures were not taken, they would agglomerate at this point upon collision. This is prevented either by adding small amounts of a "suspension stabilizer" or by employing as the dispersing medium a liquid of adjusted density and viscosity. Among the suspension stabilizers listed in the literature are finely divided insoluble inorganic compounds (*e.g.*, talc), inorganic and organic colloids (*e.g.*, gelatin), and soluble high polymers, both natural and synthetic (*e.g.*, polyvinyl alcohol). If the stabilizing agent works, polymerization continues and the drops pass beyond the sticky phase and become hard without agglomerating upon collision. When the reaction is complete, the polymerized product is in the form of *pearls* and does not have to be recovered by coagulation. The stabilizer is of such nature that it is readily removed from the surface of the pearl by simple washing; and since no emulsifying or coagulating agents have been added the product is considerably freer of impurities than one normally recovered from emulsion polymerization.

427. Copolymerization. The polymers listed in Tables 4-2 and 4-3 are all commercially important and of themselves represent a notable contribution to industry. But through copolymerization the horizons of application are greatly broadened. Almost any monomer listed in

these tables may be copolymerized with many of the others. Vinyl monomers may also be copolymerized with diene monomers to produce synthetic rubbers of great importance. The basic requirements are that the conditions *under* which and the rates *at* which two monomeric species will polymerize be reasonably similar. If there is too great a disparity in rates the more rapid compound will polymerize first and separately. Even when two monomers copolymerize successfully, the composition

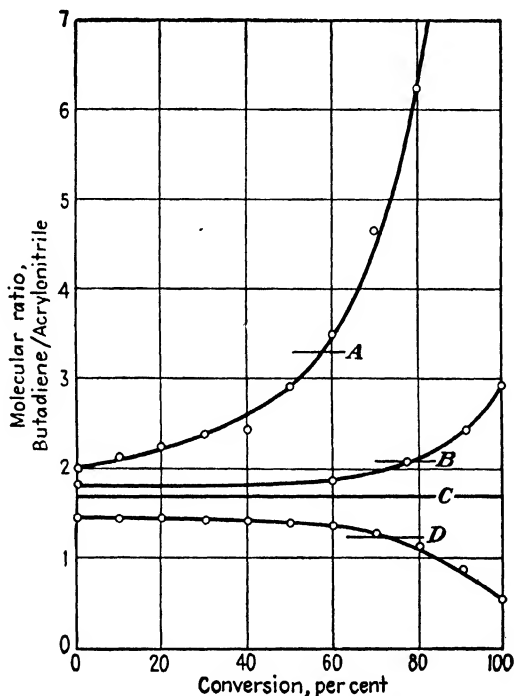


FIG. 4-8. Composition of butadiene-acrylonitrile polymer formed at any instant as function of starting composition and amount of conversion. Starting molecular ratios: A 3.28, B 2.09, C 1.67, D 1.25. [W. L. Semon, *Chem. Eng. News*, **24**, 2900 (1946).]

of the polymer does not necessarily correspond with that of the starting mixture of monomers, nor does the composition of the chains first formed correspond with that of the chains formed later (Fig. 4-8). This important behavior serves to explain why, in some systems, only limited ranges of copolymer compositions are produced commercially. Reasonable homogeneity must be preserved in the product, or its properties may prove inferior. This heterogeneity in composition, not mentioned till now, contributes toward the internal plasticizing effect.

428. General Properties of Vinyl Polymerization Products. Vinyl polymerization products are generally linear and thermoplastic. As a

group, they soften at low temperatures. Most of them cannot withstand a continuous operating temperature of 100 C. They are eminently suited for injection molding and extrusion and, indeed, all the techniques suited to thermoplasts (Chap. 8). Some, notably the acrylic resins, are well adapted to casting. Those which are completely hydrocarbon in character, especially polyethylene and polyisobutylene, lean toward rubberiness and have excellent dielectric properties. All can be extruded with sufficient external plasticizer.

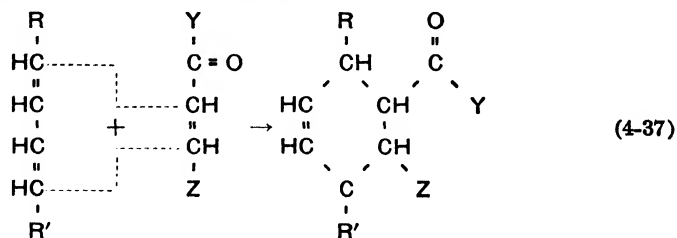
Many can be oriented by elongation under tension or unidirectional rolling to an extent where they exhibit well-defined x-ray patterns (Fig. 5-29). Analysis of their x-ray and electron diffraction photographs is thus helpful in establishing their structures. Fiber periods are listed in Table 5-3. A few, notably polyvinyl chloride-acetate (Table 3-3) and Saran (Fig. 2-12), have been drawn into fibers of commercial consequence.

They all transmit light and vary from translucence to exceptional clarity, reaching a peak of excellence in the acrylic resins. Many of the commercial products are both internally and externally plasticized. Considered as a family, they are very numerous and find applications in plastics, rubbers, surface coatings, adhesives, fibers, and textile-treating agents. Since they are highly thermoplastic, they are not generally suited to the production of high-strength laminates.

POLYMERIZATIONS INVOLVING CONJUGATED UNSATURATION

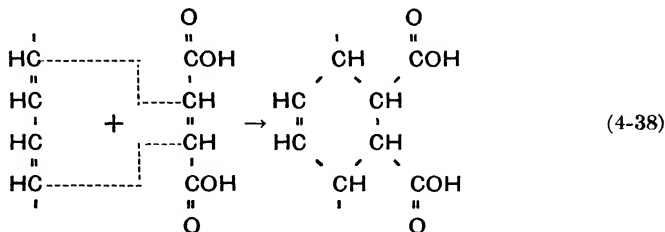
Compounds containing conjugated double bonds are chemically reactive and potentially tetrafunctional. Bond shifts may occur in several different ways. Consequently, their chemical behavior is complex, and their reactions are often difficult to control.

429. The Diels-Alder Reaction. The well-known Diels-Alder reaction or diene synthesis is a cyclizing addition reaction and takes place between a compound containing conjugated olefinic double bonds and another containing a —C=C—C=O group.



The significance of this reaction may be gathered from the following example. Assume that it occurs between a multifunctional chain polymer

containing conjugated bonds and a dicarboxylic acid or anhydride containing a —C=C—C=O group, *e.g.*, maleic or phthalic acid or anhydride.

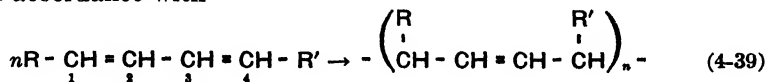


The carboxyl groups introduced on the main chain now make it possible for condensation reactions to take place with appropriate reactants such as alcohols. If a glycol, glycerol, or other highly functional alcohol is employed, condensation involving cross-linkage between the main chains can occur. Thus it is possible to synthesize highly complex resins that are at one and the same time addition and condensation polymers. As desired, they may be more or less polar in character, they may possess extremely poor molecular symmetry, and they may be more or less highly cyclized. The possible ramifications in structure and chemical composition are practically unlimited. Manufacture of resins of this nature requires precise control of conditions.

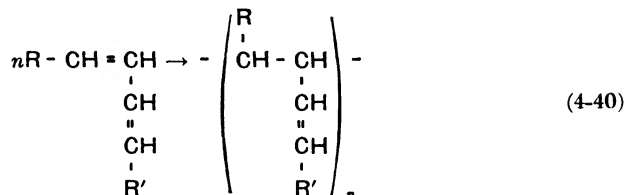
The Diels-Alder reaction requires a conjugated diene. It is often possible to start with an unconjugated diene and still obtain the reaction because of a preliminary rearrangement of bonds in the diene in accordance with Eq. (4-27, page 119).

In passing, it is interesting to note why complex polymers of the type just discussed are useful in surface coatings. A surface coating must not form cracks since these rob it of its protective ability and act as focal points for film breakdown (Sec. 1423). A surface-coating polymer should therefore exhibit little tendency to crystallize after the coating has been applied since crystallization involves densification and may result in minute cracks. Highly internally plasticized molecules do not crystallize readily and are thus inherently suited for surface-coating purposes. Furthermore, cyclic structures are generally more resistant to solvents and reagents than analogous uncyclized structures. Hence the polymers under discussion are likely to form surface coatings of high durability.

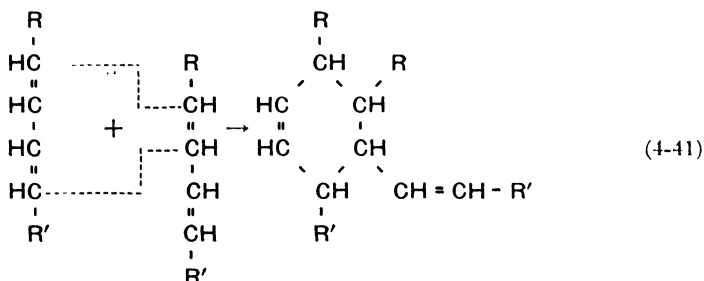
430. Diene Polymerizations. Although it is potentially tetrafunctional, under proper conditions a conjugated diene monomer may behave bifunctionally and polymerize by 1,4 addition into multifunctional linear chains in accordance with



It is also capable of vinyl polymerization.



It can likewise undergo dimerization by what is called a *modified Diels-Alder reaction*.

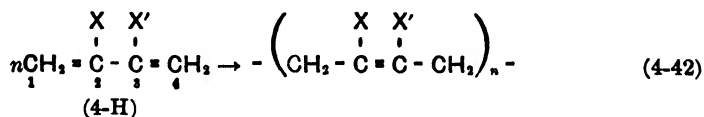


This cyclizing addition involves 1,4 conjugation of one structure and a vinyl addition of the second. Obviously, if the two diene structures were on different chains, this reaction would result in cross-linkage.

When a conjugated diene monomer is being polymerized, these reactions (and still others) are competitive. Besides catalytic effects, the course of the reaction is strongly influenced by temperature and the number and kind of substituents on the terminal carbon atoms (meaning carbons 1 and 4 of the conjugated diene structure). High temperatures and substituent groups (R and R'), especially large ones, favor dimerization via Eq. (4-41), while low temperatures and hydrogen atoms on carbons 1 and 4 are conducive to polymerization [Eqs. (4-39) and (4-40)].

Drying-oil glycerides contain conjugated structures with terminal substituents that are large alkyl radicals (Table 14-1). Reaction (4-41) is prominent in drying-oil polymerization.

At the current writing the most important dienes from the standpoint of synthetic polymer production are 1,3-butadienes representable by the general structure (4-H); their polymerization in accordance with Eq. (4-39) is



In commercial practice the X's are more usually hydrogens, chlorines, or methyl groups but may be other substituents as well. Various diene polymers formed via Eq. (4-42) are shown in Table 4-7. Insofar as they

TABLE 4-7. POLYMERS FORMED FROM MONOMERS OF TYPE $\text{CH}_2=\overset{\text{X}}{\underset{|}{\text{C}}}-\overset{\text{X}'}{\underset{|}{\text{C}}}=\text{CH}_2$

—X	—X'	Monomer	Polymer
—H	—H	$\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{CH}_2=\text{C}-\text{C}=\text{CH}_2 \\ \text{1,3-Butadiene} \end{array}$	Polybutadiene
—CH ₃	—H	$\begin{array}{c} \text{H}_3\text{C} \quad \text{H} \\ \quad \\ \text{CH}_2=\text{C}-\text{C}=\text{CH}_2 \\ \text{Isoprene} \end{array}$	Polyisoprene
—CH ₃	—CH ₃	$\begin{array}{c} \text{H}_3\text{C} \quad \text{CH}_3 \\ \quad \\ \text{CH}_2=\text{C}-\text{C}=\text{CH}_2 \\ \text{2,3-Dimethyl-1,3-butadiene} \end{array}$	Polydimethylbutadiene, or methyl rubber
—Cl	—H	$\begin{array}{c} \text{Cl} \quad \text{H} \\ \quad \\ \text{CH}_2=\text{C}-\text{C}=\text{CH}_2 \\ \text{Chloroprene} \end{array}$	Polychloroprene, or neoprene

are linear multifunctional unsaturated polyhydrocarbons, they resemble *cis*-polyisoprene, the hydrocarbon of Hevea rubber (Table 1-4), and their main use is as synthetic rubbers. In producing these rubbers, 1,4 addition in accordance with Eq. (4-42) is the preferred reaction. However, many less desirable concurrent reactions are likewise possible, among them

1. 4,4 and 1,1 addition, *i.e.*, head-to-head and tail-to-tail as well as the preferred head-to-tail addition
2. Formation of both *cis* and *trans* units (Table 1-1)
3. Vinyl polymerization [Eq. (4-40)]
4. The modified Diels-Alder reaction [Eq. (4-41)]

These side reactions reduce the quality of the products. The last two result directly or indirectly in cross-linkage of the main chains, thus "pre-vulcanizing" the materials and rendering mastication and the incorporation of compounding ingredients difficult. The conflicting reactions also result in molecular symmetry of such a low order that these rubbers do not crystallize on stretching (Fig. 5-18) and hence do not attain the high tensile strengths exhibited by those which do (Sec. 1319). It is therefore essential to repress side reactions and promote reaction (4-42) as far as possible during manufacture.

431. Control of Diene Polymerizations. Much of the discussion of Secs. 420 *ff.* applies to diene as well as vinyl polymerizations. Butadiene rubbers may be polymerized in bulk, using metallic sodium as catalyst.

(They were first called *buna* rubbers, the name being a combination of the first syllable of butadiene and the chemical symbol for sodium. A newer and better name is *buta* rubbers since sodium catalyst is no longer employed.) Owing to the high viscosities developed during polymerization and the inherently poor heat-transfer characteristics of these hydrocarbons, control over the reaction is not good, and the final products are nonuniform and of poor quality.

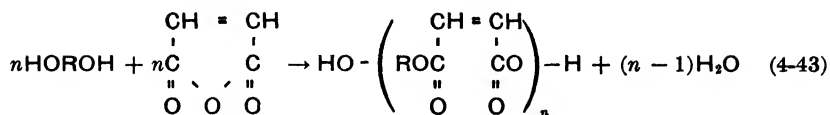
Much better results are obtained when emulsion polymerization is employed. Catalyst combinations have been discovered that not only promote reaction (4-42) but also inhibit undesirable side reactions. A typical diene emulsion-polymerization batch (Table 13-3) contains both polymerization catalysts and orientation catalysts. It has also been found that, in accordance with the discussion of Sec. 415, the introduction of polar groups on carbons 2 and 3 of the butadiene monomer [structure (4-H)] speeds polymerization and exerts a directive effect favoring reaction (4-42). For example, chloroprene, $\text{CH}_2=\text{CCl}-\text{CH}=\text{CH}_2$, polymerizes more rapidly and yields straighter chains than butadiene. In 2,3-dichlorobutadiene, $\text{CH}_2=\text{CCl}-\text{CCl}=\text{CH}_2$, the effects are still more marked.

432. Copolymerization. Butadiene monomers may often be copolymerized with one another, *e.g.*, chloroprene with isoprene. Furthermore, a diene monomer may be copolymerized with a suitable vinyl monomer. Thus, copolymers of butadiene and styrene are known as *buta S* (*buna S*) and those of butadiene and acrylonitrile, $\text{CH}_2=\text{CH}-\text{CN}$, as *buta N rubbers*. These latter are also called nitrile rubbers. Other vinyl monomers can be and are used, the copolymerization enhancing the properties of the product.

Polyisobutylene (Table 4-3) is a rubbery material with many highly desirable properties, but since it contains no functional groups, it cannot be vulcanized. By copolymerizing isobutylene with appropriate amounts of a diene such as butadiene or isoprene, double bonds are introduced on the chains, and vulcanizable *butyl rubbers* are produced.

433. Carbon-Oxygen Conjugation. It has been stated that two conjugated structures of the type $-\text{C}=\text{C}-\text{C}=\text{C}-$ may combine in a modified Diels-Alder addition [Eq. (4-41)]. Similarly, a $-\text{C}=\text{C}-\text{C}=\text{C}-$ structure can combine with a carbon-oxygen conjugated structure, $-\text{C}=\text{C}-\text{C}=\text{O}$, via the regular Diels-Alder reaction [Eq. (4-37)]. It evidently is also possible for two carbon-oxygen conjugated structures to add to one another, perhaps by a mechanism similar to those above mentioned.

If maleic anhydride is reacted with a glycol under oxygen-free conditions, linear thermoplastic polyesters form by condensation polymerization.



When exposed to air, especially in the presence of oxygen-yielding catalysts, these polyesters are converted into tough, hard, insoluble, infusible resins that give all evidence of being space polymers. The cross-linking reaction is accomplished with no elimination of water and appears to be effected solely through addition polymerization involving $-\text{C}=\text{C}-\text{C}=\text{O}$ structures that are activated by oxygen.

Evidently carbon-oxygen conjugated unsaturation may behave much like conjugated diene unsaturation in affording functional centers for addition polymerization and cross-linkage.

A strong correspondence between the $-\text{CH}=\text{CH}-\text{CH}=\text{CH}-$ and $-\text{CH}=\text{CH}-\text{C}=\text{O}$ structures is further indicated by the fact that films of glycol maleate polyesters [Eq. (4-43)] not only possess air-drying properties similar to those of natural drying oils but also undergo similar surface wrinkling during oxygen conversion.

Also of considerable interest is the fact that glycol maleate and similar esters containing carbon-oxygen conjugation are soluble in various vinyl monomers and when the solution is heated (with a peroxide) copolymerization takes place. The resulting products possess characteristics of both condensation and addition polymers. Depending on temperature, relative concentrations, catalyst, etc., the properties of a particular product vary according to which of three competing polymerizations predominate, *viz.*, (1) addition polymerization of the vinyl monomer with itself; (2) addition polymerization of the glycol maleate with itself (cross-linkage); (3) addition polymerization between the two (copolymerization).

CHEMICAL MODIFICATION OF HIGH POLYMERS

434. New polymers may be produced by chemical modification of high polymers. Such modification is rarely carried out on synthetic polymers, for the desired end product may usually be produced directly by polymerizing the appropriate monomers to begin with. An exception is polyvinyl alcohol, which is made by the hydrolysis of polyvinyl acetate since the hypothetical monomer, vinyl alcohol, is nonexistent. In turn, the technically important polyvinyl acetals are formed by reacting aldehydes with the indirectly prepared polyvinyl alcohol [Eq. (10-22), p. 464].

The high polymers of widest distribution and lowest cost are those occurring ready made in nature, *e.g.*, silicates, cellulose, and proteins. Accordingly, the most important instances of high-polymer modification are those conducted on natural polymers.

The structure of a natural polymeric raw material is a *fait accompli*. The objective during chemical manipulation is normally to preserve the ready-made main structure of the chains while modifying their properties to suit specific needs. To this end, the reactions to which the material is subjected may be divided into two broad classes, (1) reactions involving chain rupture (degradation); (2) reactions involving chemical modification, *e.g.*, addition, substitution, oxidation, or reduction.

Reactions of the first class change mainly the molecular size and affect solubility, solution viscosity, plasticity, strength, and, indeed, all those physical properties which are functions of the degree of polymerization and size distribution. Reactions of the second class change the molecular shape, symmetry, and polarity, and besides affecting the physical properties they also change the chemical behavior. A derivative with a particular set of desired properties is usually produced by combining chain rupture with chemical modification, *i.e.*, by changing both the D.P. and the D.S. The production of suitable derivatives of a natural polymer therefore requires adequate control over these various reactions. This control is often complicated, for reasons now to be discussed.

Not all parts of an insoluble polymer will react simultaneously, and the reaction product may therefore lack uniformity. Many natural polymers are insoluble owing to primary-valence cross-linkage, as in wool, or exceptionally extensive hydrogen bridging, as in cellulose. Consequently, the reaction mixture used for manufacturing a natural polymer derivative often constitutes a heterogeneous system. The exterior reacts before the interior. Substitution or addition occurs at random so that partial conversion to the new chemical form reduces the recurrence symmetry and tends toward molecular nonuniformity. Furthermore, reaction usually takes place more rapidly in amorphous regions than in crystallites. Indeed, reaction may take place only in amorphous regions and on crystallite surfaces and not at all within crystallites. Such reactions are called *nonpermutoid* to distinguish them from the more homogeneous reactions, which take place inside crystallites as well. The latter are known as *permutoid reactions*. In the light of the above, the discovery and development of suitable swelling and dispersing agents for a natural polymer are commonly a problem of major importance.

Natural polymers are at their maximum average chain length when taken from the original source, and the physical and chemical manipulations to which they are subjected normally cause more or less degradation, whether such degradation is desired or not (Table 4-8). Often a reduction in chain length is desirable in order to obtain proper solution or flow characteristics in the products. At times, as in the milling and compounding of Hevea rubber, extensive damage due to overmuch degradation

is practically unavoidable. In such cases, mechanical strength may sometimes be restored by cross linking the degraded chains into stronger space-polymerized structures. Indeed, this is absolutely essential for the production of good rubber products.

TABLE 4-8. AVERAGE DEGREES OF POLYMERIZATION OF VARIOUS CELLULOSIC MATERIALS AND DERIVATIVES

Material	Degree of Polymeri- zation from Solution- viscosity
	Measurements
Native cotton.....	3,500
Purified cotton linters.....	1,400
Sulfite pulp.....	1,000
Mercerized cotton.....	2,000
Cellulose acetates.....	175-370
Cellulose acetate-butyrate.....	250-350
Regenerated celluloses (rayons).....	250-600
Cellulose nitrate for blasting gelatin.....	3,000
Cellulose nitrate plastics.....	500-600
Cellulose nitrate, $\frac{1}{2}$ -sec lacquer grade.....	175
Alpha-cellulose.....	>200
Beta-cellulose.....	10-200
Gamma-cellulose.....	<10

REACTIONS OF CELLULOSE

435. Cellulose and cellulosic fibers afford an excellent basis for illustrating the problems and fundamental procedures of natural polymer manipulation.

Cellulose fibers are the main constituents of cotton, flax, hemp, jute, ramie, wood, etc. In cotton fibers, cellulose occurs almost pure, but in all other important natural cellulosic materials it is associated with sizable amounts of impurities including lignin, a natural resin, and various hexosans, pentosans, and polyuronides collectively known as *hemicelluloses*. It is beyond the scope of this discussion to detail these impurities, but their presence and the fact that they may exert powerful influences on fiber properties must be kept in mind. The starting materials for the manufacture of chemical derivatives of cellulose are purified fibers from either cotton linters or specially processed wood pulp high in alpha-cellulose or so-called "true" cellulose content.¹

¹ That portion of a sample of "cellulose" which does not dissolve after a 45 min treatment with a 17.5 per cent aqueous solution of NaOH at 20 C is called the *alpha-cellulose content*. What does dissolve is arbitrarily divided into two kinds, *beta-cellulose*, which reprecipitates upon neutralization of the filtrate with acid, and *gamma-cellulose*, which does not.

Both the molecular and gross structure of the cellulosic raw material are important determinants of its behavior (Secs. 524 *ff.*). The cellulose molecule, which is strictly linear and strongly polar, is shown in structure (5-E, page 206).

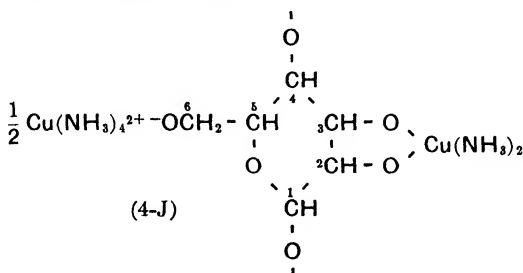
436. Swelling and Dispersion. Water swells a native cellulose fiber considerably but does not dissolve it. No change in the x-ray pattern accompanies the swelling. The reaction is of the nonpermutoid type. The water molecules solvate the amorphous regions (Fig. 2-9) and the surfaces of the crystallites but do not penetrate or break down the crystallites. The swelling in water and, indeed, in all swelling agents, is anisotropic and takes place at right angles to the fiber axis rather than along it.

The effects of solutions of electrolytes are more extensive. Thus, if a cellulose fiber is immersed in an aqueous solution of caustic alkali at proper temperature and concentration, swelling is accompanied by changes in the x-ray spot pattern. Ions of the reagent are found to have penetrated the crystallites, and ionized mers have formed on the cellulose chains. In other words, addition compounds called *alkali celluloses* have formed, and the reaction is of the permutoid type. For example, at room temperature a 13 to 19 per cent NaOH solution appears to lead to the formation of glucoside anions, $C_6H_5O_5^-$ or $C_6H_5O_5H_2O^-$, which are balanced by sodium ions. A new x-ray spot pattern appears, and the addition compound is called *soda cellulose I*. Since they are parts of the cellulosic chain, the anions are, of course, nondiffusing. At higher alkali concentrations a different "swelling compound" called *soda cellulose II* forms, as indicated by the appearance of still another x-ray pattern. Although caustic alkalies promote profound changes in the fiber, collectively known as *mercerization* (Sec. 1144), they do not cause actual breakdown of the crystallites and the dispersion of individual chains.

Many important processes such as the manufacture of films and artificial fibers require that a liquid dispersion of suitable viscosity be prepared as the first step. Several electrolyte reagents have been found suitable for this purpose. There is considerable reason to believe that whenever actual molecular dispersion occurs it is a chemical derivative of cellulose and not cellulose itself that goes into solution.

When purified native cellulose is treated with certain quaternary ammonium bases such as tetraethylammonium hydroxide, solution takes place. Solution also occurs in cuprammonium hydroxide (Schweitzer's reagent), which contains the $Cu(NH_3)_4^{2+}$ complex, and copper-amine solutions, *e.g.*, those containing the $Cu(ethylenediamine)_2^{2+}$ complex. Although the details are not clear, it appears certain that when treated with such reagents the cellulose mers become ionic and that what goes into solution is the solvated chains of a multiionic cellulose derivative.

In the copper-ammonia and copper-amine reagents it appears likely that part of the copper enters into Werner complex formation via the hydroxyls on carbons 2 and 3 of the cellulose mer and that the cellulose is anionic since it is precipitated at the anode during electroosmosis. The structure may be of the nature shown below:



At any rate, the ionic character and poor architectural symmetry of the derivatives serve to explain their solubility in such liquids as water.

Regenerated cellulose is precipitated when a cuprammonium dispersion is treated with acid. This serves as the basis for the commercial manufacture of cuprammonium rayon (Sec. 831). Cellulose may be dispersed in Schweitzer's reagent with very little degradation. These dispersions are therefore also important in that the measurement of their solution viscosities serves as a method for determining the molecular weights of cellulosic materials.

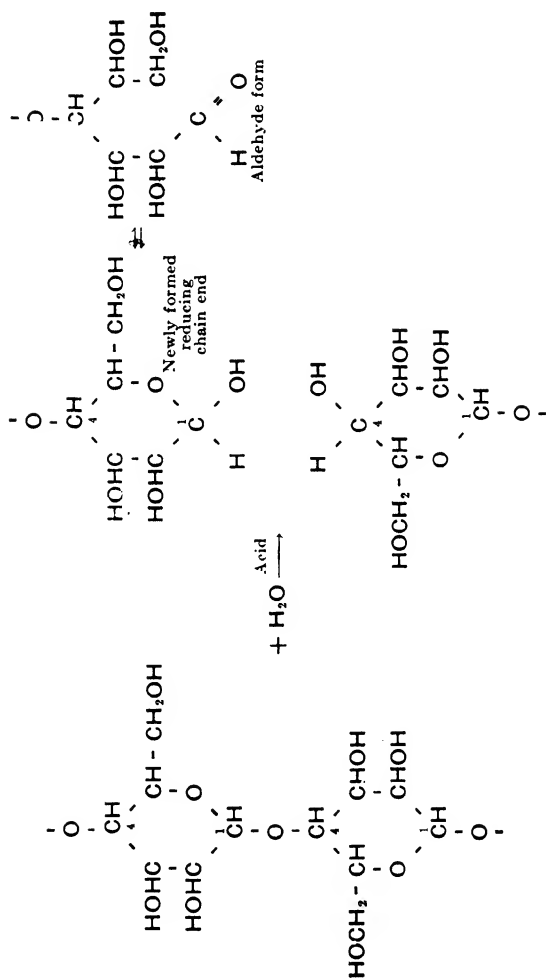
Many strong electrolytes besides the ones mentioned above act as powerful swelling or dispersing agents for cellulose, *e.g.*, concentrated zinc chloride, phosphoric acid, and sulfuric acid.

437. Degradation. The two main types of reaction involved in cellulose degradation are hydrolysis at the 1,4 linkage and oxidation. Depending on which of these predominates during processing, very different degradation products are obtained, even when the products have the same average molecular weight. These reactions are discussed briefly below.

438. Hydrolysis at the 1,4 Link. Hydrolysis of cellulose at the 1,4-glucoside link results in chain rupture [Eq. (4-44)]. The reaction is acid catalyzed and is called *hydrolytic degradation*. Even dilute solutions of weak acids at room temperature cause it. One of the two ends of a cellulose chain is aldehydic. Since with each rupture two new termini are formed, the reaction may be followed by measuring the reducing power or by measuring solution viscosities.

The insoluble degraded products of this hydrolysis are known as *hydro-celluloses*. Cellulose in fibrous form is preferentially attacked in the amorphous regions. Hence, even small amounts of hydrolysis cause an

(4-44)

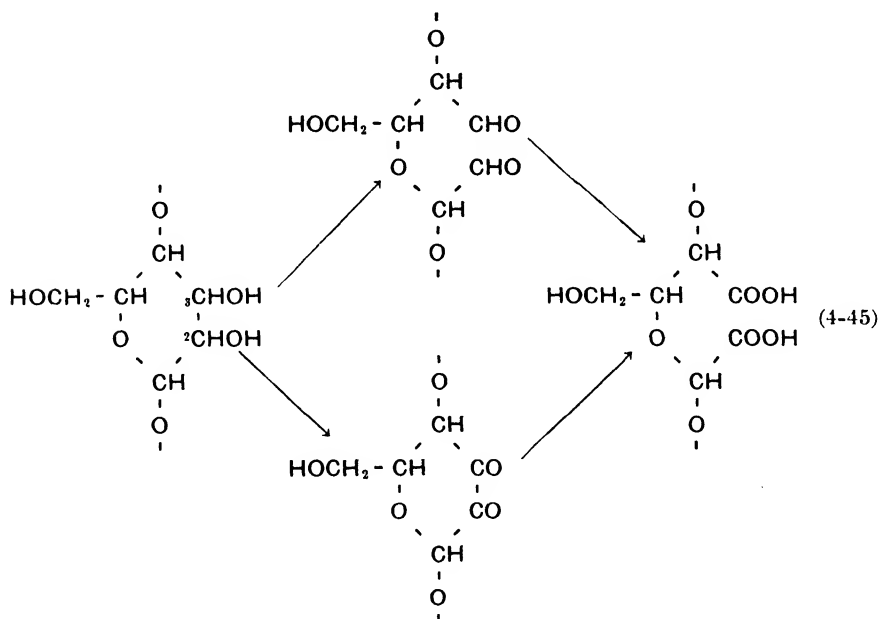


inordinate decrease in the tensile strength of a fiber. As hydrolysis progresses, the amorphous regions are destroyed first and the fiber crumbles to a powder of the more resistant crystallites. On the other hand, in homogeneous cellulosic dispersions, hydrolytic rupture appears to occur at random. It is an important fact that derivatives such as the cellulose esters and ethers are less susceptible to hydrolysis than cellulose itself, probably because of hindrance at the 1,4 linkage.

439. Oxidation. Cellulose oxidation with the ultimate formation of carboxyl groups may take place in three ways.

1. Oxidation of the primary alcohol group on carbon 6
2. Oxidation of the secondary alcohol groups on carbons 2 and 3
3. Oxidation of the ends of chains

No chain or ring rupture accompanies the first of these reactions. Only when the degree of polymerization is low does the third reaction contribute appreciably to the total carboxyl formation. The second reaction may result in ring rupture without chain rupture as shown in Eq. (4-45), where the complexity of the process is illustrated.



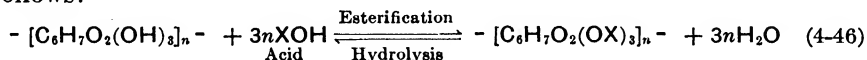
The various products of cellulose oxidation are called *oxycelluloses*. Owing to the many competing reactions and intermediate stages, their compositions are indefinite. Different oxidants exhibit specific tendencies to attack the primary or secondary alcohol groups, and the acidity of the medium also determines the course of the reaction, alkaline media pro-

moting carboxyl formation and acidic media favoring the formation of aldehydic groups resulting in so-called *reducing oxycelluloses*. The presence of carboxyl, aldehyde, and other structures in oxycelluloses accounts for their increased alkali solubility and their enhanced ability to take up basic dyes and act as metal binders.

Cellulose is particularly sensitive to oxidation in alkaline media, and oxidation in turn increases the sensitivity to hydrolysis. Consequently, combined oxidation and chain rupture, known as *oxidative degradation*, is especially likely to occur in media that are simultaneously alkaline and oxidizing. In many outstandingly important processes such as wood-pulp cooking and bleaching, textile scouring and laundering, rayon manufacture, etc., cellulose is subjected to treatment with alkali in either the deliberate or the incidental presence of an oxidant. Great care must be exercised to protect it against excessive degradation during these manipulations. Hydrolytic and oxidative degradations also accompany the deterioration of cellulosic materials by heat and light.

440. Substitution. The effects of the degree and modes of substitution on cellulose have been discussed in Sec. 236. Molecular polarity and symmetry are both altered when the alcohol groups are replaced by others. Furthermore, more or less degradation always accompanies the chemical conversion. At the current writing the most important cellulose derivatives are esters and ethers. Variation of the type of substituent, degree of substitution, and degree of polymerization yields polymers with widely different characteristics suitable as rayon fibers, plastic binders, surface-coating binders, artificial leather, adhesives, packaging films, photographic films, explosives, and substitute rubber.

441. Esterification. Commercial cellulose esters are produced by treating purified cellulose fibers with various acid reagents, *e.g.*, acids themselves, acid anhydrides, or acid chlorides. The esterification is catalyzed by mineral acids. Esterification and hydrolysis are, of course, opposite reactions and in the case of cellulose may be represented as follows:



Intermediate degrees of substitution are the usual thing. Owing to the reversibility of the reaction, total esterification is difficult to effect and in most finished products is undesirable. The final average D.S. depends on the final concentrations of both esterifying agent and water. The leftward (hydrolysis) reaction is often called *saponification*.

Acidic reagents such as those used in commercial ester production catalyze hydrolytic degradation [Eq. (4-44)]. This reaction also depends upon the activity of the water. It is kept under control or minimized

by using concentrated reagents and adding strong dehydrating agents. Concentrated sulfuric acid is often added to the reaction mixture since it both catalyzes esterification and removes water.

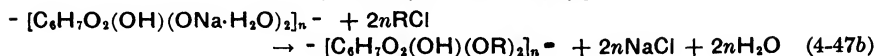
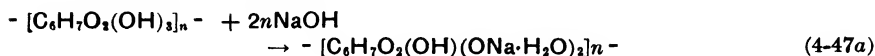
As previously noted, a mixture of cellulose fibers and liquid reactants is a heterogeneous system from which nonuniform reaction products may result. Of the commercially important derivatives only cellulose nitrate can be brought into true equilibrium with the reaction medium at points short of complete substitution. Other partly substituted cellulose esters are therefore made by first esterifying completely in order to obtain a *soluble* product, which is then hydrolyzed (saponified) back to a more uniform product of the desired D.S. This is accomplished by the judicious addition of water and reversal of reaction (4-46).

In accordance with the above discussion, the starting mixture used for making cellulose acetate contains purified cotton linters, acetic anhydride as the actual acetylating agent, glacial acetic acid to act as solvent for the acetylated cellulose, and concentrated sulfuric acid as catalyst and dehydrating agent. The average D.P. of the final product can be controlled by the molecular weight of the original cellulosic stock, the amount of degradation accompanying esterification, and treatments after esterification, *e.g.*, fractional precipitation or heating. Table 4-9 shows relations between commercial application, D.S., and D.P. for cellulose nitrates. They may be considered typical and should be compared with the data of Table 3-3, page 87.

TABLE 4-9. TYPICAL CHARACTERISTICS OF CELLULOSE NITRATES FOR DIFFERENT APPLICATIONS

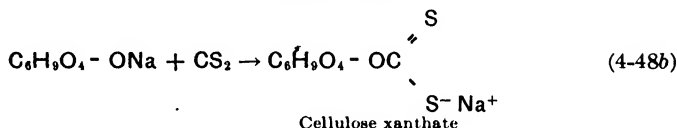
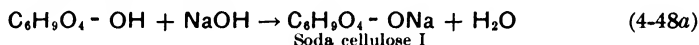
Cellulose nitrate for	Nitrogen content, wt. %	D.S.	D.P.
Plastics.....	11.0	2.0	500
Films and foils.....	11.5-12.2	2.1-2.3	275
Lacquers ($\frac{1}{2}$ -sec viscosity).....	12.0	2.25	175
Blasting gelatin.....	2.3	2.35	3,000
Smokeless powders.....	12.5-13.5	2.4-2.75	

442. Etherification. The etherification of cellulose is effected by reacting an alkylating agent with an alkali cellulose. At the current writing the usual industrial procedure is treatment of soda cellulose with an alkyl or aryl chloride in aqueous medium. Control over the D.S. is obtained by varying the relative concentrations of cellulose, water, alkali and alkylating agent. In the over-all, etherification to a D.S. of 2 may be represented as follows:



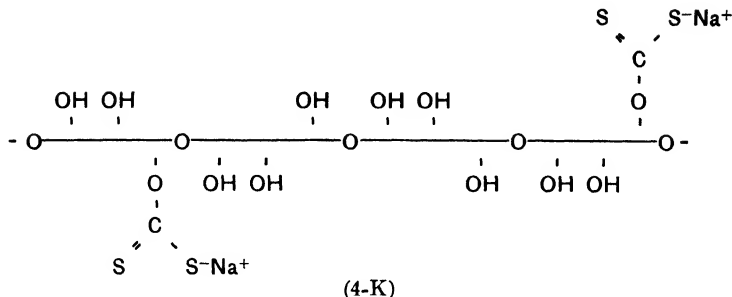
In this nonhomogeneous system the rate of alkylation depends upon the ease with which the alkylating molecules can penetrate the swollen soda cellulose, as well as upon relative concentrations. Side reactions include direct hydrolysis of the alkylating agent and oxidative degradation. The latter may be minimized by rigorously excluding air from the system. This once more illustrates difficulties encountered in working with a natural polymer.

443. Xanthation. When treated with caustic alkali and carbon disulfide, alcohols in general form xanthates. Carbon disulfide reacts with an alkali cellulose to form cellulose xanthate, an ionic high polymer that dissolves in water, yielding a viscous solution known as *viscose*.



A whole series of secondary reactions complicate and obfuscate the main reactions.

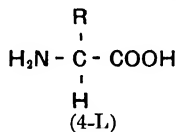
Cellulose may be precipitated (regenerated) from a viscose solution by the simple addition of acid. In this way, viscose rayon fibers and cellophane films are made, the final products in each instance consisting of regenerated cellulose. Purified cellulose fibers are first steeped in a 17 per cent NaOH solution at room conditions, forming soda cellulose I. The excess alkali is squeezed out, and the soda cellulose is allowed contact with air under controlled conditions to effect oxidative degradation. The process is called *aging*. If insufficient degradation occurs at this point, the viscose solutions prepared later are too viscous to handle readily, whereas if the degradation is permitted to go too far the tensile strength and other properties of the finished product are inferior. The properly aged soda cellulose is next treated with CS₂ to form the orange-colored water-soluble xanthate. The reaction ratio is roughly one CS₂ to two glucoside mers, which means that about one in every six alcohol groups of the original cellulose chain is xanthated (D.S. = 0.5). The xanthation reaction appears to be of the nonpermutoid type. A cellulose xanthate chain may be represented schematically by structure (4-K). The lack of molecular symmetry coupled with the ionic character serves to explain why the xanthate is soluble in aqueous media.



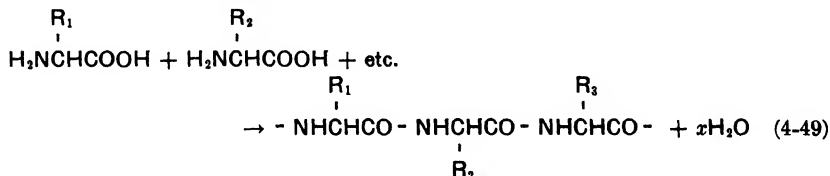
Viscose solutions are not stable. With time, xanthate groups slowly hydrolyze off, a multitude of side reactions taking place. The solution viscosity drops, passes through a minimum, and then rises again. A solution must be "ripened" to a suitable stage before it is used for generating fibers or films (Chap. 8). To make these, fine streams or thin curtains of the ripened viscose are run into an acid bath. The acid causes immediate hydrolysis and removal of all the xanthate structures that have not previously split off during ripening. The resulting regenerated cellulose precipitates in the form of continuous fibers or films.

REACTIONS OF WOOL

444. Like all proteins, wool is a natural polyamide and hydrolyzes to yield a mixture of α -amino acids with the general structure



The twenty-odd amino acids that have been isolated from various proteins differ in the $-\text{R}$ group, which varies greatly in size, symmetry, complexity, and functionality from the hydrogen atom of glycine to the bicyclic structure of tryptophane (Table 4-10). From their behavior on hydrolysis and in other chemical reactions, one may postulate that fibrous proteins such as silk and wool are composed of chain polymers formed via bifunctional condensation.¹



¹ Actually, the formation of proteins, Hevea rubber, and other natural polymers may occur via ring-scission polymerization (Secs. 418 and 419).

TABLE 4-10. AMINO ACID COMPOSITION OF SOME ANIMAL PROTEINS

Amino acid	Formula	M.W.	Silk fibroin		Wool keratin		Collagen and gelatin		Casein	
			Wt. %	Acids accounted for, Mole %	Wt. %	Acids accounted for, Mole %	Wt. %	Acids accounted for, Mole %	Wt. %	Acids accounted for, Mole %
Glycine.....	<chem>C(N)CC(=O)O</chem>	75	36.8	50.8	7	13.5	23.6	32.6	0.5	0.8
Alanine.....	<chem>C(C)C(N)C(=O)O</chem>	89	22.2	25.8	4	6.5	10.3	11.6	5.6	7.5
Serine.....	<chem>C(CO)C(N)C(=O)O</chem>	105	11.4	11.2	3.3	3.3	6.5	7.3
Threonine.....	<chem>C(C(C)O)C(N)C(=O)O</chem>	119	1.3	1.1	1.5	2.3	3.9	3.9
Valine.....	<chem>C(C(C)C)C(N)C(=O)O</chem>	117	2.7	2.4	4.5	5.6	2.5	2.3	7.0	7.1
Leucine and isoleucine.....	<chem>CC(C)C(C)C(N)C(=O)O</chem>	131	0.8	0.6	11	12.1	5.4	4.3	18.6	16.8
Proline.....	<chem>C1CCN(C1)C(=O)O</chem>	115	1	0.9	9.2	11.7	15.3	13.8	8.2	8.5
Hydroxyproline.....	<chem>C1CC(O)C(N1)C(=O)O</chem>	131	13	10.3	2	1.8
Phenylalanine.....	<chem>C1=CC=C(C=C1)C(C(N)=O)C(=O)O</chem>	165	3.9	3.4	2.0	1.3	5.2	3.7
Methionine.....	<chem>CSCC(C)C(N)C(=O)O</chem>	149	0.6	0.6	0.8	0.6	3.5	2.8
Cystine.....	<chem>SCC(C)C(N)C(=O)O</chem>	240	11.1	6.7	0.1	0.4	0.2
Tryptophane.....	<chem>C1=CC=C2C(=C1)C(=CN2)C(C(N)=O)C(=O)O</chem>	204	1.5	1.1	1.8	1.0
Tyrosine.....	<chem>C1=CC(=C(C=C1)C(=O)O)C(C(N)=O)C(=O)O</chem>	181	11.1	6.4	5.1	4.1	0.2	0.1	6.4	4.2
Histidine.....	<chem>C1=NC(=NC(=C1)C(=O)O)C(N)=O</chem>	155	0.06	0.7	0.6	1.0	0.7	2.5	1.9
Arginine.....	<chem>C1=NC(=NC(=C1)C(=O)O)C(N)C(N)C(N)=O</chem>	174	0.9	0.5	10.0	8.3	7.6	4.5	4.1	2.8
Lysine.....	<chem>C1=NC(=NC(=C1)C(=O)O)C(N)C(CCN)C(=O)O</chem>	146	0.2	0.2	3.0	3.0	4.3	3.0	6.9	5.6
Aspartic acid.....	<chem>C(C(=O)O)C(N)C(=O)O</chem>	133	7.3	7.9	8.5	6.6	6.3	5.6
Glutamic acid.....	<chem>C(C(C(=O)O)C(N)C(=O)O)C(=O)O</chem>	147	15.3	15.0	5.4	3.8	22.8	18.4

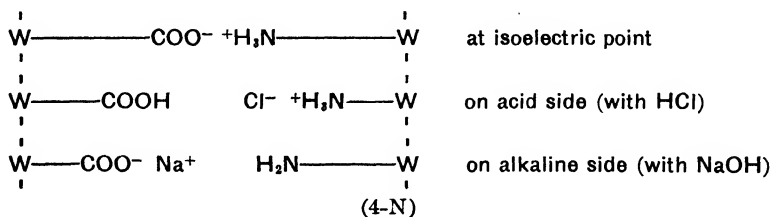
BLOCH, R. J., and D. BOLLING, "Amino Acid Composition of Proteins and Foods," Charles C. Thomas, Publisher, Springfield, Ill., 1945.

This structure is confirmed by x-ray diffraction (Secs. 528 and 529), which reveals that silk and wool have definite fiber patterns.

The proteins of wool, hair, feathers, horns, fingernails, etc., are called *keratins*. Both the molecular and the gross structure of a keratin influence its behavior. As in the case of cellulosic fibers, wool has a morphology, and it is found that the epidermis and cortex differ considerably in chemical composition as well as in structure. It is thus clear that a "keratin" is in no sense a homogeneous material, and all statements about it must be accepted and interpreted with caution.

445. Composition of Wool. Wool has the very complex composition that is typically protein. Hydrolysis yields 18 or more different α -amino acid "monomers" of highly diverse character, no one of which is present in predominant amount (Table 4-10). The wool keratin chains presumably formed by bifunctional condensation of these monomers possess very poor architectural symmetry. A hypothetical portion of a wool chain containing some of the possible amino acid residues is shown in structure (4-M). A simple calculation based on the data of Table 4-10 indicates that in these molecules only 50 per cent of the total weight is in the main—NHCHCO— chains, the other half being in the side chains (—R groups).

446. Amphoteric Nature. Like proteins in general, wool is amphoteric because of the presence of carboxyl and amino groups shown in structure (4-M). Table 4-10 reveals that over 30 mole per cent of the amino acid residues carry carboxyl or amino groups and that acidic and basic groups are present in roughly equivalent amounts. Around the isoelectric point, amphoteric ions (zwitter ions) exist that exert strong attractions upon one another, thus contributing considerably to the total interchain bridging. This is called *salt bridging*. These ionic structures are neutralized by the uptake of either acid or alkali.

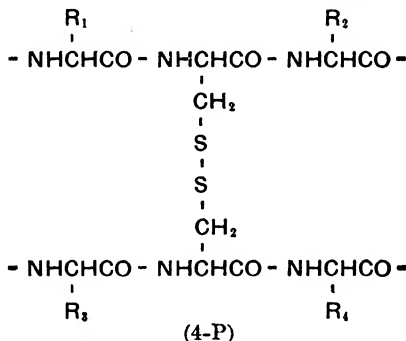


(In the above structures the symbol —W— represents a main chain of wool.) Such neutralizations should decrease the intermolecular forces of attraction, and in confirmation it has been found that, when wool fiber is permitted to react with HCl, the work of extension decreases linearly with the acid uptake until the stoichiometric amount of acid has been taken up. Further confirmation is afforded by the fact that wool, like

other proteins, is most difficult to swell with solvents in its isoelectric zone (pH 5 to 7).

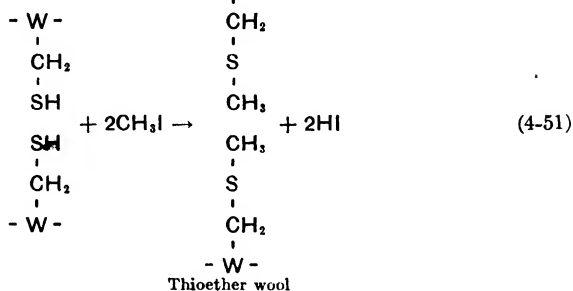
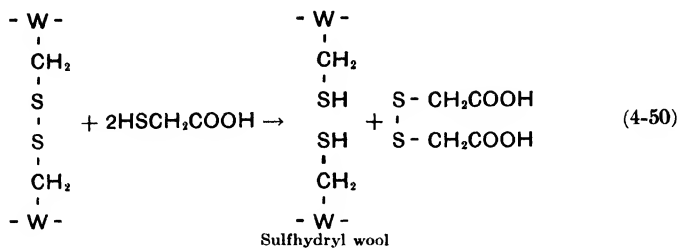
Table 4-10 shows further that some of the amino acid units of wool carry phenolic groups, while about 50 mole per cent such as glycine and leucine residues are nonfunctional. The poor molecular symmetry results in the presence of many imperfectly bridged polar groups of various sorts. These features serve to account for the ready swelling in polar solvents, the excellent uptake of dyes, etc.

447. Cross-linkage. Although the swelling of wool in polar liquids is extensive, it is limited. Solution does not take place. The presence of cystine in its hydrolysis products (Table 4-10) suggests that this limited swelling is due to primary-valence cross-linkage between the main chains since cystine is an α -amino acid at both ends and hence capable of condensing into two chains, thus serving as a tetrafunctional branch unit [structure (4-P)]. This postulate is substantiated by considerable evi-

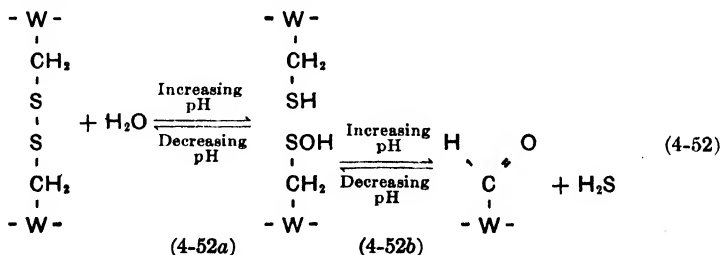


dence. A disulfide structure such as that of cystine is chemically active and readily broken down by many reagents. It is possible to analyze for cystine sulfur quantitatively and hence to follow the breakdown with exactness. The data of Table 4-10 indicate that there is enough cystine in wool keratin for about 10 mole per cent of the amino acid units to be cross-linked to one another.

If wool is treated first with the reducing agent thioglycolic acid and then with an alkyl halide, the following changes take place. The wool is greatly weakened. Its resistance to tension decreases. It shrinks readily. Indeed, its stress-strain behavior becomes strikingly like that of rubber (Sec. 909). Limited swelling is replaced by true solubility in appropriate polar liquids. These are precisely the changes that would normally accompany conversion from a cross-linked to a linear-polymeric structure. This fits in with the chemistry of the process. If the disulfide group of cystine behaves like disulfide groups in general, the treatment with the reagents cited above should break existing cystine cross-links as follows:



Normal wool fiber is readily damaged by alkalis, oxidants, reductants, light, moths, carpet beetles, etc. This accounts for many of the sad results of laundering and storage. Various studies, including the processes summarized in Eqs. (4-50) and (4-51), prove conclusively that primary-valence cystine cross-links are present in normal wool. Techniques were developed for rupturing any desired fraction of the cystine links, and it was discovered that, when wool is permanently damaged or weakened by any of the above-mentioned agencies, the attack always begins with a rupture of the disulfide groups of the cystine cross-links. For example, the primary process in attack by alkali is a hydrolytic rupture resulting in the formation of a sulfhydryl and sulfenic acid structure [Eq. (4-52a)]. The sulfhydryl group is rather stable in alkali, but the sulfenic acid is highly reactive in such media and decomposes rapidly into hydrogen sulfide and an aldehyde [Eq. (4-52b)]. The primary hydrolysis represented by reaction (4-52b)



may be effected by water alone at elevated temperatures, *i.e.*, by steam.

Since the wool fiber is not in solution while these reactions are taking place, not all the disulfide groups react simultaneously. Sulfide formed from reaction (4-52b) reduces some of the still unreacted disulfide groups directly to sulfhydryl groups. These reactions account for the fact that, when wool is treated with dilute alkali, a rapid splitting off of part of the cystine sulfur occurs, after which the sulfur content approaches a constant value of about 1.8 per cent, below which it does not drop. (Needless to say, degradation due to hydrolysis of the amide linkages of the main

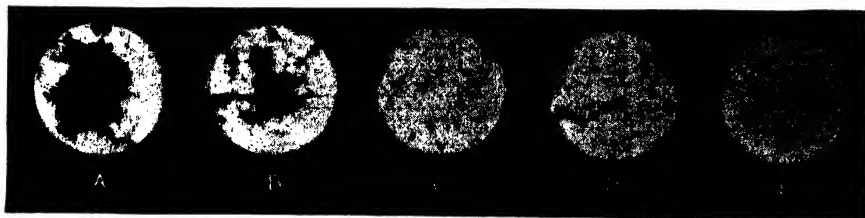
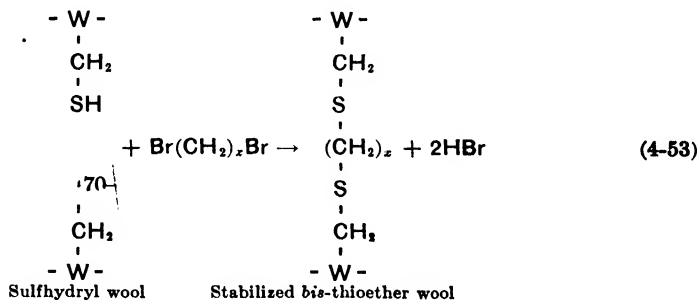


FIG. 4-9. Wool samples after exposure to black carpet beetles. A: Untreated wool. Modified wools prepared by reduction with calcium thioglycolate followed by alkylation with trimethylene bromide. B: 10% cystine. C: 6.5%. D: 4.0%. E: 2.0%. [W. B. Geiger, F. F. Kobayashi, and M. Harris, *Ind. Eng. Chem.*, **34**, 1398 (1942).]

chains also can take place. Wool keratin is particularly susceptible to this hydrolytic degradation in alkaline solutions.)

One of the commercially significant results of these investigations was the development of a method for producing a chemically stabilized wool as follows: Normal wool fiber is reduced to linear-polymeric sulfhydryl wool in accordance with Eq. (4-50). The latter is then treated with a bifunctional cross-linking agent in the form of an alkyl dihalide. The polyfunctional system then reacts to form a wool that is once again cross-linked [Eq. (4-53)].



Since the wool is again cross-linked, it has regained its original mechanical strength. Furthermore, thioethers are much more stable chemically than disulfide structures. Consequently the chemically modified wool exhibits greatly enhanced resistance to damage by chemical agents (laundering) or the destructive enzymic secretions of moths and carpet

beetles (Fig. 4-9). The reagents and reaction conditions involved in producing the stabilized wool are so mild that appearance and hand are not altered.

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See also Appendix A, particularly Sec. A-4.

PARTICULAR TOPICS

See references accompanying tables and figures of this chapter.

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PRICE, C. C., "Mechanisms of Reactions at Carbon-Double Bonds," Interscience Publishers, Inc., New York.

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See also references at end of Chap. 11.

Wool

See references at end of Chaps. 5 and 11.

CHAPTER 5

STRUCTURES OF HIGH POLYMERS

500. Since 1910 many of the great advances and contributions of physical chemistry have been in the field of structure elucidation, including the structures of atoms and molecules themselves as well as their organization in gases, liquids, and solids. A good deal of this progress has resulted from the discovery and intensive development of new experimental techniques involving the use of electromagnetic radiations. The range of such waves is given in Table 5-1. All the types listed, except perhaps γ rays, are applied in experimental investigations, the results of which are of outstanding value in the study of high polymers.

TABLE 5-1. ELECTROMAGNETIC RADIATIONS

Type of ray	Range		Method of generation
	Wave length, A	Frequency, kc	
γ (gamma).....	0.01-1.4	3×10^{17} - 2×10^{15}	Atomic disintegrations and nuclear reactions
X (Roentgen)....	0.06-1,000	5×10^{16} - 3×10^{12}	Stoppage of fast-moving electrons
Ultraviolet.....	136-3,900	2×10^{13} - 8×10^{11}	Hot bodies and ionized gases
Visible.....	3,900-7,700	8×10^{11} - 4×10^{11}	Hot bodies and ionized gases
Violet.....	3,900-4,220		
Blue.....	4,200-4,920		
Green.....	4,920-5,350		
Yellow.....	5,350-5,860		
Orange.....	5,860-6,470		
Red.....	6,470-7,700		
Infrared.....	$7,700$ - 4×10^6	4×10^{11} - 1×10^9	Heat radiations
Radio and electric waves.....	1×10^6 - ∞	3×10^9 -0	Spark discharges, oscillating electric circuits, etc.

Units: $1\mu = 10^{-3}$ mm = 10^{-6} m; $1\text{ m}\mu = 10^{-3}\mu = 10^{-9}$ m; $1\text{ A} = 10^{-1}\text{ m}\mu = 10^{-10}$ m

The particular range of waves chosen for an experimental investigation depends on the size of the structure or particle to be studied. Large particles may be examined with large waves but small ones require small

waves to be "seen." Thus, to study the gross details of a macrosurface, visible or ultraviolet light may be used (microscopy); but, to determine the location and arrangement of atoms within a mass, x rays, which are of atomic dimensions, must be employed. Another example is afforded by polarization measurements where particles must be made to oscillate. Atoms require lower frequencies than electrons, and dipoles still lower frequencies (Fig. 10-4, page 435).

OPTICS AND MICROSCOPE RESOLVING POWER

501. To the lay mind there would seem to be no limit to the tininess of particles that might be seen if one were to set up a sufficient number of powerful lenses and keep increasing the amount of magnification. However, this is not so. If magnification is not accompanied by an increase

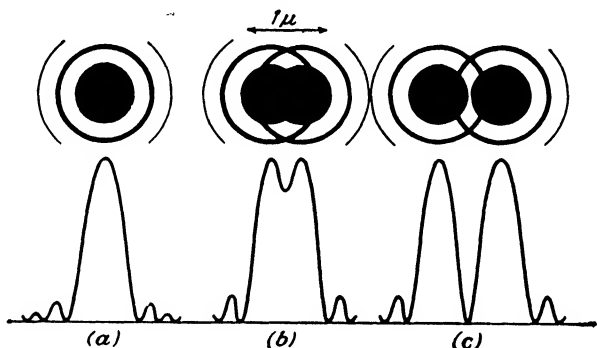


FIG. 5-1. Resolution of particles. (R. B. Barnes and C. J. Burton, *ASTM Bull.*, May 1942, p. 42.)

in "detail," no increase in what can be seen results. Rather, one merely sees what one can already see, but on a larger scale. This is empty magnification. Therefore, more fundamentally important than magnification is resolving power.

When light impinges on a point, some is absorbed and then reradiated, producing a new set of light waves, which, in an optical instrument, appears as a diffraction disk (Fig. 5-1a). The relative diameters of the central disk and the first and second bright rings are 13.4, 24.6, and 35.6. Mathematical analysis indicates that 84 per cent of the light is concentrated in the bright central part. The diameter of this diffraction disk is a function of the wave length of the incident light and the lens system of the instrument. Theoretically, two neighboring points are distinguishable from one another when they are separated by a distance such that the center of the diffraction disk of one just coincides with the first light ring of the other (Fig. 5-1b). (In actual practice, however, the points must be somewhat farther apart than this, as shown in Fig. 5-1c.) The

smaller the central disk, the less the overlapping of the diffraction patterns and therefore the better the resolving power. Without going into great detail, the *resolving power* of an optical instrument is the linear distance between two points just separable and distinguishable by the instrument. This distance is given by the formula

$$R = \frac{\lambda}{\text{N.A.}} = \frac{\lambda}{n \sin \phi} \quad (5-1)$$

where R is the resolving power, λ the wave length of light used, N.A. the numerical aperture of the lens, which equals $n \sin \phi$, n the refractive index of the medium between the object and the objective lens, and ϕ the angle between the optical axis of the system and the outermost ray caught by the objective.

If two points are closer together than R , they cannot be distinguished from one another by the instrument, *i.e.*, they cannot be "seen" separately regardless of the amount of magnification. The maximum resolving power is in direct proportion to the wave length. From Eq. (5-1) it follows that the use of short-wave radiations (*e.g.*, ultraviolet light with quartz lenses), oil immersion, and lenses of large angle ϕ , improves resolution.

With incident light nonparallel to the optical axis the resolution is somewhat better than with parallel light. For completely oblique light it is twice as great, *viz.*,

$$R = 0.5 \frac{\lambda}{\text{N.A.}} \quad (5-2)$$

With oblique light the object appears bright against a dark field (dark-ground illumination). A microscope using dark-ground illumination is sometimes called an *ultramicroscope*. Although great hopes were originally held for ultramicroscopes, they proved disappointing because the changed nature of the appearance (light object against dark field) results in a loss in detail that largely nullifies the twofold enhancement of resolution.

Table 5-2 gives the characteristics of magnifying instruments that use light. It will be seen that the limit of resolution for light microscopes is about 2,000 Å. Atom sizes and interatomic and intermolecular distances lie between 1 and 5 Å. They can neither be seen nor measured with these instruments. However, light microscopes are of tremendous value for studying the features of gross structure in polymeric materials, particularly those coming from living organisms. For example, natural fibers possess biological structure. They are not merely molecular masses. There is an organization into cell walls, cuticles, lumens, fibrils, and so on, which is best studied through light microscopes. These

features of gross organization are so important that it may be stated as a general principle that the properties and behaviors of natural fibers cannot be adequately understood without detailed knowledge of both their molecular and gross structure.

TABLE 5-2. COMPARISON OF MAGNIFIERS USING LIGHT
(Based on optical formulas and manufacturer's descriptions)

Instrument	Numerical aperture	Limit of resolution, \AA	Usual instrument magnification
Human eye.....	0.01	$1-2 \times 10^6$	1
Hand lens.....	0.1	2×10^5	10
Binocular microscope.....	0.1	5×10^4	40
Ordinary microscope.....	0.25	2×10^4	100
Research microscope.....	0.95	6,000	700
Research microscope, oil immersion objective	1.38	4,000	1,000
Research microscope, ultraviolet (2,700 \AA) objective.....	1.38	2,000	2,000

X-RAY DIFFRACTION

502. In order to resolve particles of atomic dimensions, rays of much smaller wave lengths than the ultraviolet must be employed. X rays are suitable [Table 5-1 and Eq. (5-1)]. As a result of x-ray investigations it is now known that completely amorphous solids are rare. Among low-molecular-weight substances there are very few, notably sulfur and polyhydric alcohols. Many high polymers are partly or largely crystalline; but some rubbers, proteins, and resins, particularly of the highly cross-linked synthetic variety, are to all intents amorphous. Finally, it has been discovered that some high polymers which are amorphous in the unstressed state attain crystallinity when stretched (Secs. 231 *ff.*). By means of x rays it is often possible to establish the complete structure of a crystalline material, locating the positions of the atoms as well as their orientation with respect to one another.

503. Scattering and Reflection of X Rays. As in the case of light, when a beam of x rays strikes a mass, some of the energy is absorbed by the atoms and then reradiated, the amount for any particular atom being proportional to the number of its extranuclear electrons. If the atoms within the mass are in disorder, *i.e.*, if the material is amorphous, the reradiated rays are scattered haphazardly and to a considerable degree quenched. But from matter organized in plane surfaces, *i.e.*, a crystal, regular reflection of the x-ray beam takes place. From elementary optical considerations it can be shown that, when reflection occurs, the angle of incidence equals the angle of reflection, as in the case of visible

light. With visible light, however, most of the energy is absorbed in the first layer of atoms so that the waves reflected from a plane surface contain most of the original energy of the incident beam. On the other hand, x rays, owing to their small wave length, penetrate all substances deeply. The depth of penetration depends both on the wave length of the rays and the composition of the substance. Therefore with x rays relatively little of the incident energy is absorbed by any one layer so that the reflected waves will be strong only if a number of layers combine their reflection trains in such a way that they reinforce each other. This

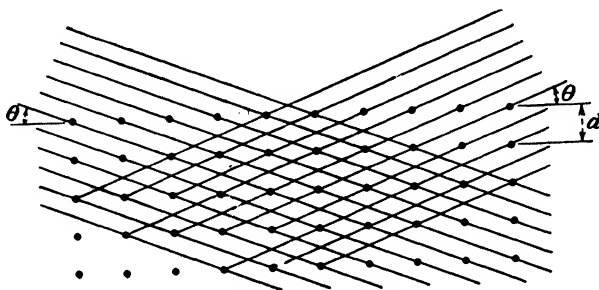


FIG. 5-2. Diffraction of a plane wave by a crystal.

introduction of "height" into the reflection phenomenon is of fundamental importance. Since the reflection from the second layer must have traveled a greater distance than the one from the first, reinforcement of the wave will take place only if the second ray arrives a full wave length (or other whole number thereof) behind the first. In a crystal, atoms are arranged in well-organized planes. The effect upon x rays is indicated in Fig. 5-2, where the dots represent individual atoms.

From geometry it is readily proved that the condition for the production of a reinforced reflected (or, as more commonly termed, diffracted) beam is met when

$$n\lambda = 2d \sin \theta \quad (5-3)$$

where λ is the wave length of x rays, d the distance between atomic planes, θ the grazing angle of incidence, *i.e.*, the angle between incident x rays and atomic plane, and n an integer—1, 2, 3, etc.

This equation is known as *Bragg's law*. To obtain a diffracted beam there must be a combination of the wave length λ and the angle θ that satisfies this equation. In one experimental method, λ is varied and θ is held constant; but in all the other methods, monochromatic x rays of constant wave length are used and it is the angle θ that varies. In all cases, however, n must be an integer. At angles that do not satisfy Bragg's equation the x rays reflected from successive layers do not arrive in phase and consequently interfere with and quench each other. With

amorphous matter, as previously stated, the radiation is scattered uniformly in all directions, and no reinforced beam results.

The magnitude of the effect described by Bragg's law obviously depends upon the number of layers of atoms contributing to the reflected beam. Modern x-ray equipment is capable of detecting order and arrangement when the crystal is as little as five atomic layers thick. In such cases, however, the diffracted beam is very wide because of incomplete quenching at angles other than θ . As the number of layers increases, *i.e.*, as the crystal becomes thicker, the diffracted beam becomes sharper.

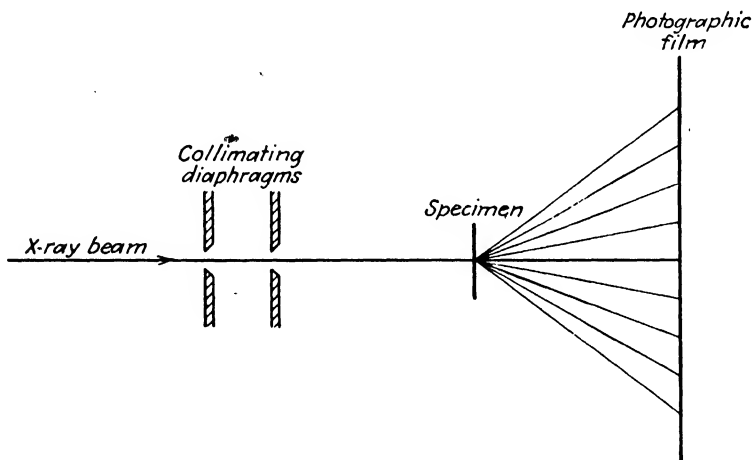


FIG. 5-3. Diffraction of x rays by a material. Curved film often used. The various x-ray methods differ as follows: (a) Laue: heterogeneous x rays, stationary single crystal. (b) Rotation: homogeneous x rays, rotating single crystal (axis of rotation in plane of paper.) (c) Powder: homogeneous x rays, stationary crystal powder. (d) Fiber: homogeneous x rays, stationary fiber bundle (axis of fiber in plane of paper).

504. Methods of X-ray Analysis. Some materials can be in the form of sizable single crystals. Others cannot. The x-ray method selected for a particular investigation depends upon the nature and physical form of the specimen and the type of information desired.

505. The Laue Method. A well-formed crystal is required as the specimen. In this method, a beam of heterogeneous x rays is used and the crystal is held stationary (Fig. 5-3). In other words, θ is constant and each set of crystal planes selects from the heterogeneous beam the particular wave length λ necessary to satisfy Bragg's law and give a reinforced beam. A typical Laue photograph is shown in Fig. 5-4. The very prominent central spot is caused by the main (undiffracted) x-ray beam. Sometimes an absorbing disk (target) is employed to avoid formation of this spot. At other times a hole is punched in the film to allow the beam to pass through without striking and consequently fogging the film.



FIG. 5-4. Laue diffraction pattern of a NaCl crystal. (Courtesy of G. L. Clark.)

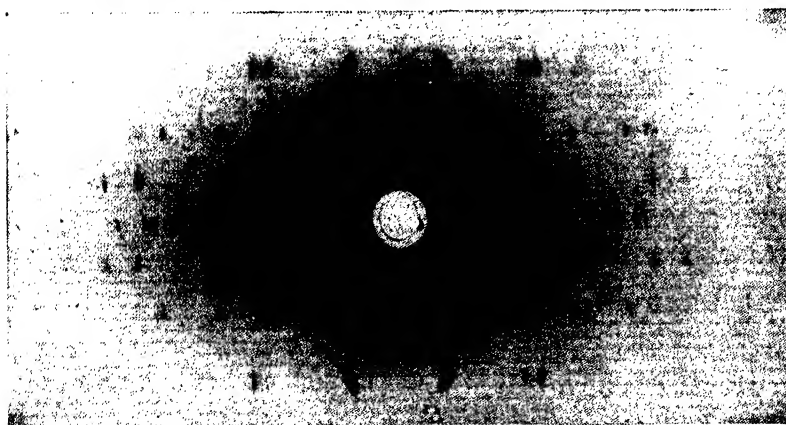


FIG. 5-5. Rotation diffraction pattern of $C_{29}H_{50}$ on cylindrical film. [A. Muller, *Proc. Roy. Soc. (London)*, **A 120**, 437 (1928).]

506. The Rotating-crystal Method. In the rotating-crystal method, a beam of monochromatic (homogeneous) x rays is used. As in the Laue method, a well-defined, single crystal is required as specimen. To bring out the various reflection planes, the crystal must be rotated (Fig. 5-3).

In other words, since in this case λ is fixed, θ must be varied to satisfy Bragg's law. Figure 5-5 shows a rotation diffraction photograph. (Although the intensity of an individual ray can be determined by photometric examination of the spot, a more exact evaluation is obtained by admitting the ray into an ionization chamber or Geiger counter.)

When the axis of rotation is parallel to an axis of the crystal or perpendicular to a crystal face, the spots are on definitely ordered "layer lines." Consequently, the crystal is usually reoriented until such layer-line diagrams are obtained. Figures 5-6a and 5-6b are schematic diagrams of photographic patterns produced by this method, in the first

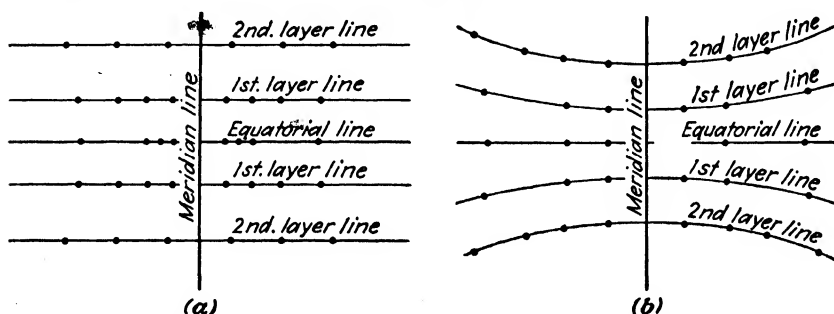


FIG. 5-6. Schematic rotation diffraction patterns. (a) On cylindrical film. (b) On plane film.

case the film being cylindrically disposed with respect to the crystal, in the second case the film being flat. Each pair of layer lines (above and below the equatorial line) corresponds to one set of planes in the crystal oblique to the axis of rotation, whereas each pair of spots on the equatorial line (on each side of the center) corresponds to one set of planes parallel to the axis of rotation.

507. The Powder Method. When no large crystal is available, the powder method is used. Monochromatic x rays are employed, and the setup is once again essentially illustrated by Fig. 5-3. The powder specimen consists of a multitude of randomly disposed, extremely minute crystals. In this method, λ is fixed, but the ray picks out the crystals lying at the proper angle θ to satisfy Bragg's law. Individual crystals in this mass therefore produce typical spot patterns; but since the crystals lie at all possible angles, these patterns are produced on the film, also, at all possible angles. As a result, the photograph consists not of spots but of continuous, concentric rings, each of uniform intensity. A typical powder-type photograph is shown in Fig. 5-7a.

A complete powder photograph therefore consists of concentric rings, each of uniform intensity and corresponding to one set of crystal planes. However, since the pattern is symmetrical about the center, it is common

practice to arrange the apparatus and film so as to photograph a band to or through the center. This practice permits the use of smaller camera and film without sacrifice of dispersion. The film in this arrangement is usually curved.

On examining liquids or amorphous solids, an x-ray diffraction "pattern" like that of Figs. 5-18a and 5-18c is obtained. Gases give similar photographs on sufficiently long exposure. Such patterns, typical of disordered, amorphous materials, consist of one or more diffuse halos, or interference rings, which on negatives appear as fogging and on positives as background darkening.

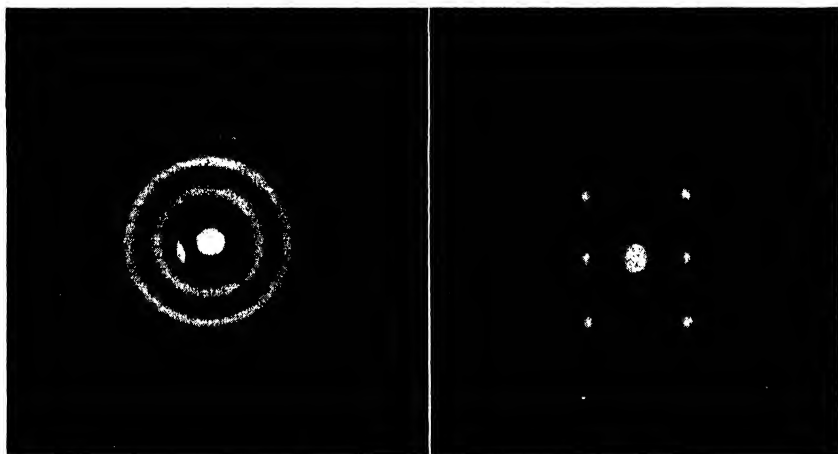


FIG. 5-7. X-ray diffraction patterns of polyvinylidene chloride. (a) Powder pattern of spontaneously crystallized material. (b) Fiber pattern of cold-drawn material. [W. C. Goggin and R. D. Lowry, *Ind. Eng. Chem.*, **34**, 327 (1942).]

If small crystals or crystallites in a solid mass are randomly disposed, the solid shows a typical "powder" diagram (Fig. 5-7a). However, if there is some preferential alignment along a particular axis such as may be induced by drawing or rolling, concentric rings of *nonuniform* intensity are obtained. Indeed, if the degree of preferential crystal or crystallite alignment is sufficiently high, the "rings" become discontinuous and resolve into concentrically disposed arcs or even spots similar to those of a typical rotation pattern (Fig. 5-7b). Patterns of this type are often obtained from high-polymer fibers, stretched rubbers, and films (Figs. 5-18b, 5-29, and 5-35). This leads the discussion directly to the fiber method.

508. The Fiber Method. The distinguishing feature of the fiber method is the nature and method of mounting the sample. The specimen consists of a small bundle of fibers that have been combed into a parallel

arrangement. The bundle is then mounted with its fiber axis vertical. A homogeneous x-ray beam is used (Fig. 5-3).

Any high-polymer mass whose molecules or crystallites can by drawing be caused to orient along a preferred (fiber) axis will yield a fiber pattern whether or not the material is normally produced and used as a fiber. Natural rubber has a fiber pattern in the stretched state (Fig. 5-18*b*). Conversely, if crystallization and preferred orientation cannot be induced, no fiber pattern is obtainable.

Some fiber photographs of synthetic linear polymers are shown in Fig. 5-29. It will be seen that the fiber pattern is similar to that produced by rotating a single crystal. It will be recalled that the object of rotating a single crystal is to allow all the crystal planes to form dif-

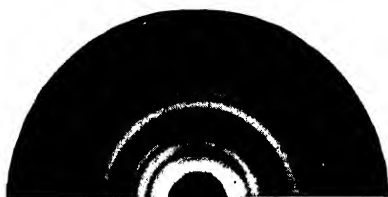


FIG. 5-8. Fiber diffraction pattern of oriented cellulose acetate-butyrate. X-ray beam *parallel* to fiber axis. (Courtesy of W. O. Baker and N. R. Pape, Bell Telephone Laboratories.)

fraction spots. With a fiber bundle, rotation of the specimen is not necessary, for, within the fibers, individual chain molecules lie in all possible positions of rotation with respect to the main bundle axis. That such random arrangement does indeed exist is shown by the fact that, if a fiber bundle is placed so that the x-ray beam passes *along* the main axis instead of *across* it as

normally, a typical "powder" diagram of complete concentric rings is obtained (Fig. 5-8). The fiber diagram is further discussed later.

509. Interpretation of X-ray Diffraction Photographs. X-ray diffraction does not yield a photographic likeness of the material. Instead, there is obtained a set of geometric projections of the individual atoms and atomic planes in space. In other words, "photography" is replaced by a set of intricate "mechanical drawings" from which the structure in space must be deduced. Full interpretation of x-ray patterns is therefore a complicated task involving considerable mathematical analysis. A detailed discussion of these calculations does not properly belong in this text.

By studying a diffraction photograph it is possible to work out a list of interplanar distances and reflection intensities from which interatomic distances, valence angles, and the crystal system to which the material belongs may be deduced. The extent of analysis possible depends on the number of lattice-plane distances that may be determined and the accuracy with which relative reflection intensities may be measured. Only for a well-formed crystal can the structure be completely resolved. However, even the meager amount of information given by the halo of a

liquid or amorphous solid allows calculation of the distance between molecules.

Crystals are built up of a fundamental unit that contains the atoms in the same proportions as they appear in the chemical formula of the compound. This minutest crystal, or *unit cell*, is a parallelepiped and is taken to contain as few atoms as possible consistent with the requirement that the real crystal can be built up by repetition of unit cells, all identical and similarly oriented.

The first object of x-ray measurement is to determine this unit cell, its size, shape, and arrangement. For a substance that forms a well-defined crystal the shape of the unit cell is given by the shape of the crystal itself, but for other substances it must be determined solely from the x-ray analysis. (The crystallites of high-polymer masses do not possess well-defined faces or uniform size.)

The number of atoms or molecules within the unit cell of a low-molecular-weight substance is usually small, but in exceptional cases very large values are obtained. Thus, rhombic sulfur has 128 atoms in its unit cell and can be made amorphous as a direct consequence of this fact. On chilling molten sulfur rapidly, the atoms are frozen into an amorphous structure, receiving no opportunity to assume their proper positions in the complicated space-lattice.

Once the unit cell has been determined, the next step is to attempt to locate the several atoms in their proper positions within the cell. This is a much more difficult process, for there are 230 possible types of arrangement, known as *space groups*. However, this analysis may be accomplished if sufficient measurements of sufficient accuracy can be made.

The fundamental measurement involved in all this work is the determination of identity periods. The distance at which parallel crystal planes or, for that matter, any regularly repeating structures appear in the crystal *with regard to a particular axis* is the *identity period* along that axis. In Fig. 5-9 the identity period I of a set of parallel crystal planes with respect to the fiber axis (or rotation axis) is shown. The relationships between this identity period, the incident x-ray beam, the reflected beam, the angle θ between these beams and the plane causing reinforcement, the angle μ ($= 2\theta$) between the reflected and incident beam, and the interplanar distance d are likewise indicated. It can be proved from this figure that the Bragg equation reduces to

$$I = \frac{n\lambda}{\sin \mu} \quad (5-4)$$

From Eq. (5-4) it is evident that *short periods result in large values of μ* , thus producing spots on the photographic film at relatively large distances

from the center of the diagram. Conversely, long periods produce spots close to the center.

Structures repeating regularly along the fiber or rotation axis produce diffraction spots vertically above and below the equatorial line (layer lines), whereas identity periods at right angles to the fiber axis produce diffraction spots to the right and left of the meridian line (row lines). The result is a network of cross spectra. Figure 5-5 is a rotation photo-

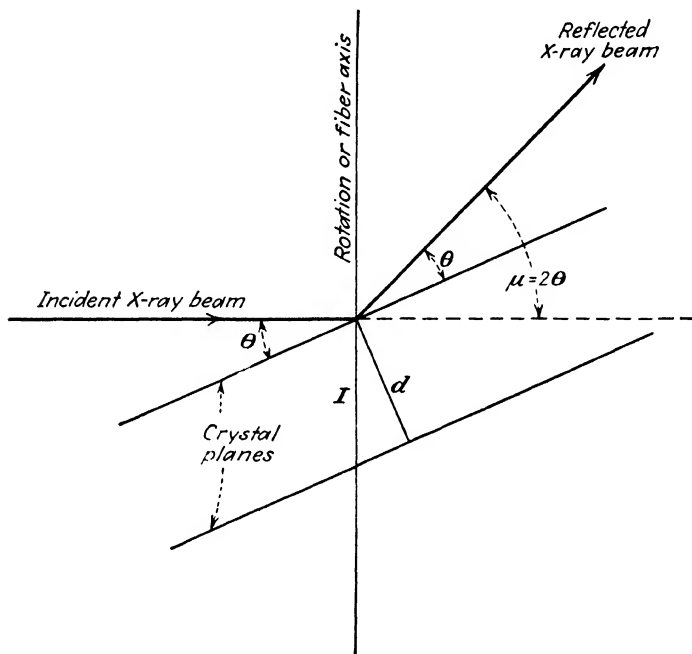


FIG. 5-9. Disposition of x-ray beams and distances in formation of x-ray fiber-diffraction pattern.

graph with layer lines and row lines perpendicular to each other, a result obtained with an orthorhombic unit cell arranged so that the rotation axis is parallel to one of the crystal axes and with the photograph made on cylindrical film. In such case the indexing of the spots is very simple.

X-ray analysis has confirmed the familiar structural formulas of carbon compounds arrived at by the organic chemist from chemical evidence. The simplest organic molecules are the normal paraffin hydrocarbons. These compounds form crystals in which the molecules are planar zigzag structures packed like rods of elliptical cross section. An x-ray diffraction pattern of such a compound is shown in Fig. 5-5. The measured carbon-to-carbon angle and distances are shown in Fig. 9-1. The angle confirms the organic chemist's concept of a tetrahedral carbon

atom. This spatial arrangement forms the backbone of most aliphatic compounds. However, the carbon atoms are not always located in a plane. In some series of compounds the carbon-carbon chains form spirals (Fig. 5-31).

In low-molecular-weight paraffin hydrocarbons the molecules in a crystal arrange themselves parallel to one another as in Fig. 5-10*a*. In this case the unit cell has a length of one molecule. If a polar group is introduced at one end of the molecules, the polar groups in neighboring molecules associate via secondary valence bridging. Thus, the normal fatty acids arrange themselves into a crystal like that of Fig. 5-10*b*. In this case the unit cell has a length of two molecules.

In many cases the molecular chains in the crystals of aliphatic compounds are perpendicular to the planes containing the ends of the molecules, *e.g.*, in hydrocarbons and alcohols. But in other cases, usually owing to a directional effect of the dipole vector, the molecular chains are tilted as shown in Fig. 5-10*b*. The same substance may exist in several crystalline modifications with different angles of tilt.

X-ray patterns of benzene and its derivatives show that the carbon atoms of the ring lie in one plane with a C—C distance of 1.42 Å. However, if there are aliphatic side chains on the ring, the carbon atoms in these chains lie at the aliphatic C—C distance of 1.54 Å. In saturated rings such as cyclohexane the C—C distance is also 1.54 Å but the ring is puckered. For double- and triple-bonded atoms the bond lengths are smaller (Table 2-1, page 27).

Despite the fact that the x-ray patterns of high polymers are often not nearly so sharply defined as those of low-molecular-weight crystals, there are certain gross features of any x-ray photograph that may be interpreted by superficial inspection. These are (1) the sharpness of the pattern, *i.e.*, the sharpness of the spots or rings, (2) the intensity of the pattern, and (3) the amount of diffuse radiation in the background. Item 1 is an indication of the degree of perfection of orientation in the crystallite fractions. Item 2 is a measure of the amount of crystalline material, while item 3 indicates the amount of amorphous material. In Chap. 2 the statement was made that fibrous masses contain both crystal-

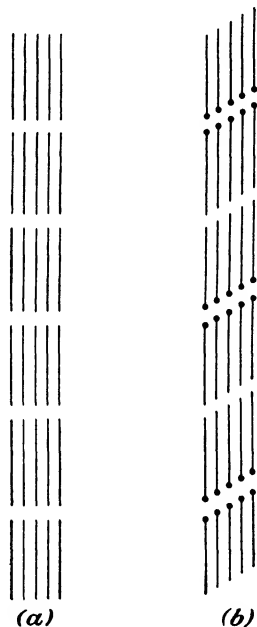


FIG. 5-10. Arrangement of molecules in normal aliphatic compounds. (a) Hydrocarbons. (b) Fatty acids.

lite and amorphous regions, and their structure was represented schematically by Fig. 2-9. The basis for this statement, among other things, is the fact that all fiber photographs show both an arc or spot pattern and a certain amount of diffuse radiation in the background, in other words, a crystal pattern superimposed on amorphous halos.

When a stress-crystallizable polymer is subjected to progressive stretching, the arcs or rings of the original pattern foreshorten and grow more intense, the fiber diagram more nearly approaching the spot pattern of a perfect crystal. Simultaneously, the intensity of amorphous halos or background diffusion decreases. These changes as they occur in a typical artificial fiber material (rayon) are shown in Fig. 5-35. They prove that, during the stretching or drawing, crystalline structures are formed at the expense of disordered or amorphous material. Attending the orientation are the changes described in Sec. 231. (See also Tables 9-2 and 9-3.) Similar changes accompany the stretching of Hevea rubber (Figs. 5-18a and 5-18b), but they are reversible, the rubber retracting to the amorphous condition when the tension is released. Buta S rubber molecules align during stretching; but, owing to their poor symmetry, crystallization does not take place (Figs. 5-18c and 5-18d).

At first only the spot patterns of fiber photographs were studied because they were so immediately apparent. Now, however, the intensity of the background radiation is also measured. The relative intensities of the pattern and the background afford a semiquantitative measure of the relative amounts of crystalline and amorphous material in the specimen.

Owing to the complexity of most high-polymer structures and the fact that single crystals are rarely obtainable, relatively few high-polymer unit cells have been completely worked out. Most of the investigations have been made on fibers since they are of a higher order of crystallinity than plastics or rubbers. But even fibers, since they are crystalline only in one direction, are suited mainly for determining identity periods *along the fiber axis*. The length of a repeating unit along the fiber axis is called a *fiber period*. A knowledge of fiber periods (Table 5-3) is highly informative in deducing molecular structure even when the complete unit cell has not been determined. Often they serve as a method of identification and analysis where all other methods fail. Many linear high polymers have several fiber periods, showing that more than one structure repeats regularly along the main axis. If there is but one fiber period, the latter is equal to the length of the unit cell along the fiber axis. If there are several, the length of the unit cell has to be the lowest common multiple of these fiber periods.

The fiber diagrams of most organic high polymers exhibit a pair of very prominent spots, or *doublets*, on the equatorial line (Fig. 5-29d). These are caused by the spacing between neighboring parallel chains.

TABLE 5-3. IDENTITY (FIBER) PERIODS OF LINEAR HIGH POLYMERS

Polymer	Mer	Fiber period, A	Probable no. of mers per period
Elastomers:			
Ethylene.....	$-\text{CH}_2-$	2.53	2
Butadiene.....	$-\text{CH}_2\text{CH}=\text{CHCH}_2-$	5.0	1
Hevea rubber, <i>cis</i>	$-\text{CH}_2\text{C}(\text{CH}_3)=\text{CHCH}_2-$	8.2	2
Gutta-percha, α <i>trans</i>	$-\text{CH}_2\text{C}(\text{CH}_3)=\text{CHCH}_2-$	8.9	2
Gutta-percha, β <i>trans</i>	$-\text{CH}_2\text{C}(\text{CH}_3)=\text{CHCH}_2-$	4.8	1
Chloroprene (neoprene).....	$-\text{CH}_2\text{CCl}=\text{CHCH}_2-$	4.8	1
Isobutylene.....	$-\text{CH}_2\text{C}(\text{CH}_3)_2-$	18.6	8
Ethylene tetrasulfide (Thio-kol A).....	$-\text{CH}_2\text{S}_2-$	8.8	2
Other vinyl-derivative polymers:			
Vinyl alcohol.....	$-\text{CH}_2\text{CHOH}-$	2.52	1
Vinyl chloride.....	$-\text{CH}_2\text{CHCl}-$	5.0	2
Vinylidene chloride.....	$-\text{CH}_2\text{CCl}_2-$	4.7	2
Glycol-dibasic acid polyesters:			
2-4 ester.....	$-\text{O}(\text{CH}_2)_2\text{OOC}(\text{CH}_2)_2\text{CO}-$	8.3	1
2-6 ester.....	$-\text{O}(\text{CH}_2)_2\text{OOC}(\text{CH}_2)_4\text{CO}-$	11.7	1
2-7 ester.....	$-\text{O}(\text{CH}_2)_2\text{OOC}(\text{CH}_2)_5\text{CO}-$	31.2	2
2-8 ester.....	$-\text{O}(\text{CH}_2)_2\text{OOC}(\text{CH}_2)_6\text{CO}-$	16.7	1
3-8 ester.....	$-\text{O}(\text{CH}_2)_3\text{OOC}(\text{CH}_2)_5\text{CO}-$	33.5	2
Cellulose and its derivatives:			
Cellulose.....	$\begin{array}{c} \text{CHOH}-\text{CHOH} \\ \diagdown \quad \diagup \\ -\text{CH} \quad \text{CH}-\text{O}- \\ \diagup \quad \diagdown \\ \text{CH}-\text{O} \\ \\ \text{CH}_2\text{OH} \end{array}$	10.3	2
Methyl cellulose.....	Above, with alcohol groups replaced by others	10.3	2
Cellulose acetate.....		10.3	2
Cellulose ethyl oxalate.....		15.4	3
Cellulose nitrate.....		25.6	5
Synthetic polyamides (nylons):			
6-6 amide.....	$-\text{HN}(\text{CH}_2)_6\text{NHOC}(\text{CH}_2)_4\text{CO}-$	17.4	1
9-9 amide.....	$-\text{HN}(\text{CH}_2)_9\text{NHOC}(\text{CH}_2)_7\text{CO}-$	24.0	1
10-10 amide.....	$-\text{HN}(\text{CH}_2)_{10}\text{NHOC}(\text{CH}_2)_8\text{CO}-$	25.6	1
Natural polyamides (protein) fibers:			
Silk fibroin.....	$-\text{NHCHRCO}-$	7.0	1
Wool and hair.....	α -keratin	5.1	
	β -keratin	6.8	

Data from several sources, notably MARK, H., in "Chemistry of Large Molecules," BURK and GRUMMITT, editors, Interscience Publishers, Inc., New York, 1943.

Since small identity periods result in large scattering angles and widely spaced spots, they are easily and accurately measured. In carbon compounds the smallest possible fiber period is 2.5 Å (Table 5-3 and Fig. 9-1). For large periods the diffraction spots are close together and close to the central spot. Hence they cannot be measured so accurately.

The crystallites in a high polymer fiber may be several hundred angstroms long. A serious difficulty in the measurement of very long periods is the obscuring of spots by the undeviated x-ray beam which, as a result of scattering by the air, target, and photographic plate, produces a dense haze around the center of the film. These difficulties may be partly overcome by increasing the specimen-to-film distance (which moves the diffraction spots away from the center) and by locating the target between the specimen and the film (which decreases the haze produced by air and target scattering).

A special method for investigating the large identity periods produced by micelles is to deposit minute crystals of heavy metals in the interior of the material. A convenient manner of accomplishing this is to impregnate the material with a solution of gold or platinum salts and then precipitate the metal by reducing agents or ultraviolet radiation. The solution penetrates the intermicellar spaces and amorphous material but does not penetrate the micelles themselves. As a result of this technique the micelles become surrounded and outlined by heavy metal atoms. The latter, having great x-ray scattering power, enhance greatly the diffraction spots produced by the large identity periods and facilitate their measurement against the background haze around the central spot.

ELECTRON MICROSCOPY AND ELECTRON DIFFRACTION

510. Electrons and other particles in motion have wave properties. The wave length of a moving particle is given by De Broglie's equation,

$$\lambda = \frac{h}{mu} \quad (5-5)$$

where h is Planck's constant, m the mass of the particle, and u the velocity of the particle.

Experiments have confirmed the wave nature of a stream of electrons, and a natural outcome of this discovery was the development of electron microscopy and electron diffraction.

511. Electron Microscopy. Several different types of electron microscope have been developed. Although a stream of electrons is a radically different kind of illumination, it is used much in the same fashion as light. In ordinary light microscopes, the light is condensed, passed through a thin object, and then magnified by an objective and one or two stages of

image magnification. Analogously, in electron microscopes a beam of electrons is condensed, passed through a thin object, and then magnified by an objective and one or two stages of image magnification. The magnification and focusing in electron microscopes are accomplished by magnetic fields, electrostatic fields, or both. These fields change the path of the electrons in much the same way as an optical lens changes the path of light rays. Indeed, they are termed *electron lenses*.

By imposing an appropriate accelerating potential (30,000 volts is common in electrostatic types) it is possible to make electrons move with enormous velocity so that the electron beam has a very short wave length [Eq. (5-5)]. De Broglie's equation may be rewritten in terms of accelerating potentials as follows:

$$\lambda = \frac{K}{E^{1/2}} \quad (5-6)$$

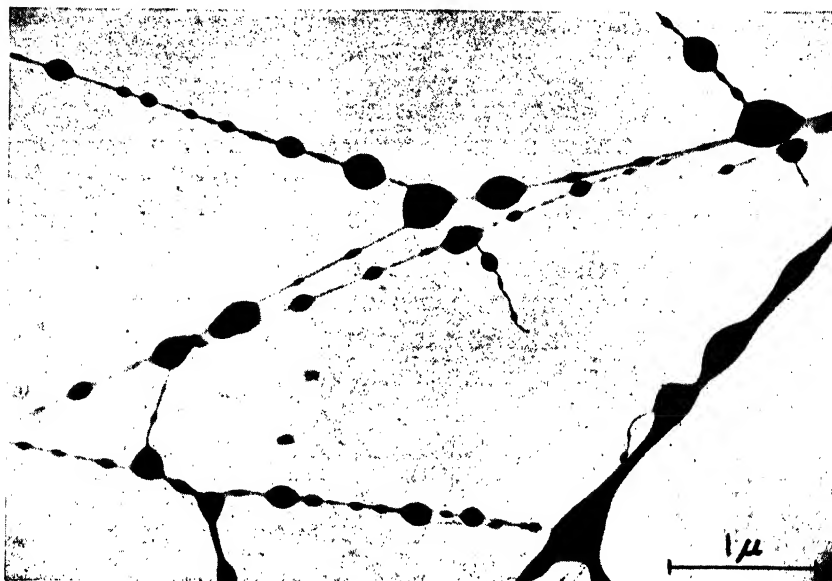
where K is a constant and E the accelerating potential. Since it is readily possible in practice to attain effective wave lengths of 0.5 Å, 10,000 times smaller than that of visible light, a useful magnification 10,000 times greater than that of the best light microscope is potentially possible [Eq. (5-1)]. Actually, however, to get the necessary sharp focusing a much smaller numerical aperture must be used. The net result is a practical limit of resolution of 40 Å, which is nevertheless 100 times better than that of the best white-light microscope and 50 times better than that of an ultraviolet microscope (Tables 5-2 and 5-4). While this

TABLE 5-4. ELECTRON MICROSCOPES (AMERICAN-MADE)
(Based on optical formulas and manufacturer's descriptions)

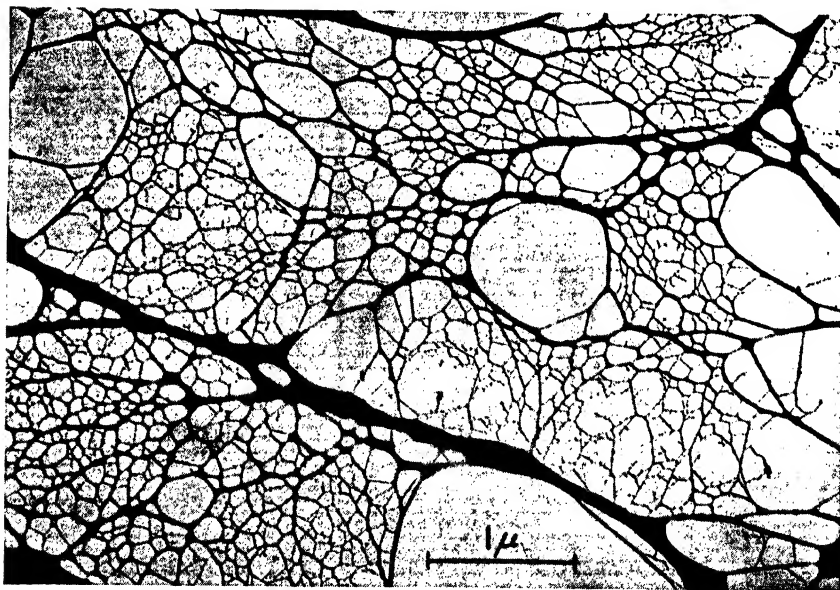
Instrument	Limit of resolution, Å	Usual instrument magnification
Electrostatic type, General Electric.....	200	4,000
Electromagnetic, RCA type C.....	100	5,000
Electromagnetic, RCA type U.....	40	20,000

is still not good enough to enable us to "see" individual atoms or small molecules, it is a great stride in that direction. Many crystallites are larger than 40 Å. If and when methods are discovered for making suitable aberration corrections in electron lenses, it may be possible to see individual small molecules. Electron-microscope pictures are shown in Figs. 5-11, 5-12, and 11-11.

The construction and use of an electron microscope present certain difficulties. Since electrons are easily stopped and have little penetrating



(a)



(b)

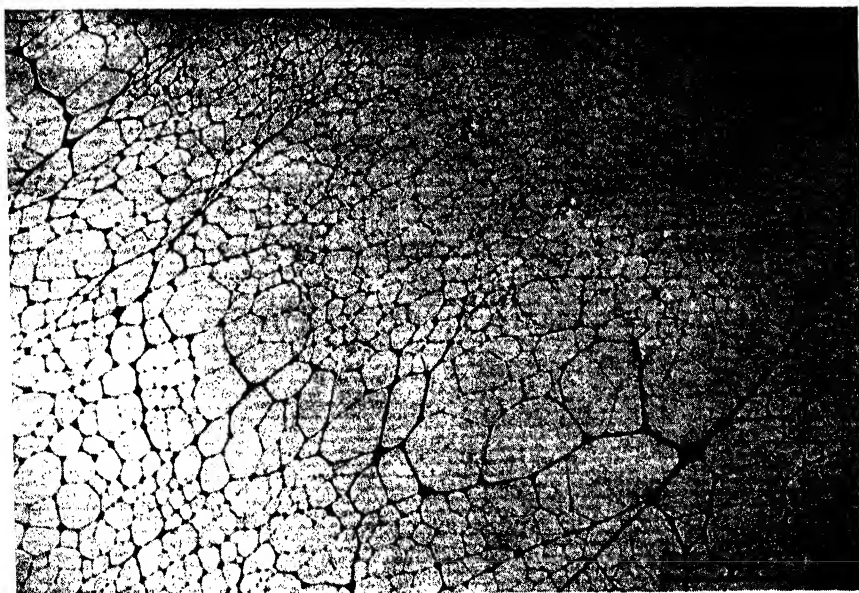
FIG. 5-11. Electron-microscope photographs of Hevea rubber drawn into tendrils ($\times 20,000$). (a) Unvulcanized sol fraction. (b) Unvulcanized gel fraction. (c) Milled

power, the entire microscope must be evacuated and only very thin objects can be studied. Also, considerable heat is produced in an object while it is under observation, and thus heat-sensitive materials cannot be readily examined.

512. Electron Diffraction. Although electron diffraction is applicable to the structure investigation of most forms of matter, owing to the greater experimental difficulties it is at present used only when x-ray diffraction is inadequate.

The penetrating power of x rays is so great that x-ray diffraction cannot be used for studying very thin films. There is too little reinforcement of the diffracted beams. Conversely, electron beams show so little penetrability that electron diffraction is unsuitable for studying solids of appreciable thickness but is ideal for the examination of gases, films, and thin layers (Fig. 5-12).

A beam of electrons passed through a thin film produces a pattern very like the corresponding x-ray pattern. For example, an oriented solid produces a typical fiber diagram (Fig. 5-13). Analysis of the patterns is exactly analogous to that of x-ray patterns. That the results of the two methods are practically identical may be seen from the data in Table 5-5.



(c)
and then vulcanized in solution. [C. E. Hall, E. A. Hauser, *et al.*, *Ind. Eng. Chem.*, **36**, 634 (1944).]

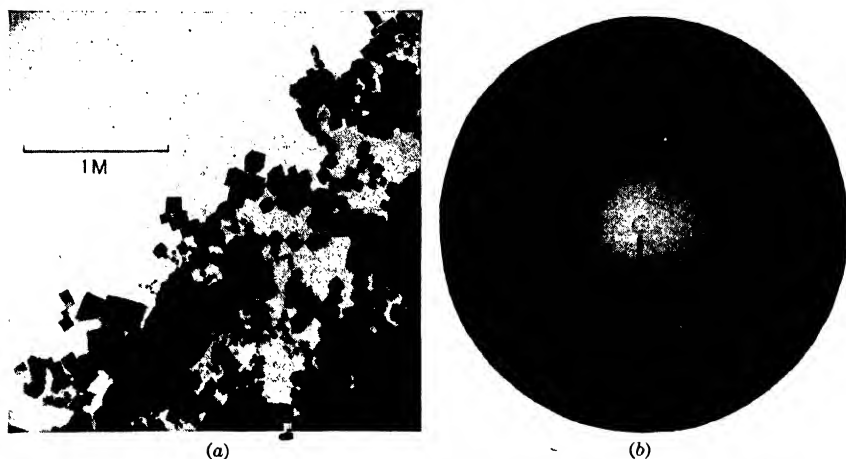


FIG. 5-12. Electron photographs of same sample of magnesium oxide. (a) Electron-microscope picture ($\times 20,000$). (b) Electron-diffraction pattern. (Courtesy of RCA Manufacturing Co.)

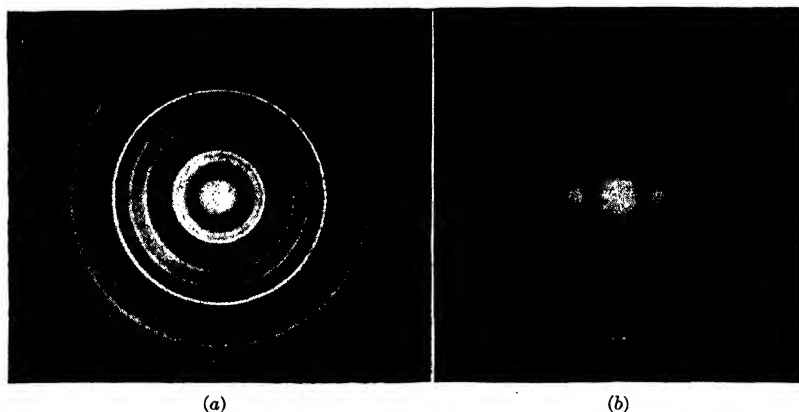


FIG. 5-13. Electron-diffraction patterns of polyethylene sebacate. (a) Unstretched (b) Stretched. [K. H. Storks, *J. Am. Chem. Soc.*, **60**, 1753 (1938).]

TABLE 5-5. COMPARISON OF ELECTRON AND X-RAY-DIFFRACTION FIBER-PERIOD MEASUREMENTS

Substance	Fiber periods, Å	
	Electron diffraction	X-ray diffraction
Polyethylene succinate.....	8.42	8.32
Polyethylene adipate.....	11.91	11.71
Polyethylene sebacate.....	16.92	16.67

STORKS, K. H., *J. Am. Chem. Soc.*, **60**, 1753 (1938).

PHASE CHANGES AND TRANSITION EFFECTS

A transition from one state to another is accompanied by various changes in physical and thermodynamic properties. It is the careful study of these changes that has lent new insight into the structure of matter.

513. The Nature of First-order Transitions. At the melting point of a crystalline solid or the boiling point of a liquid, a change in volume

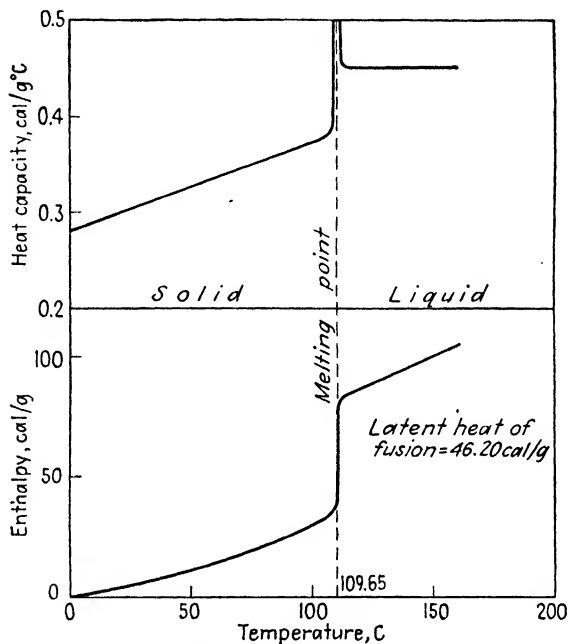


FIG. 5-14. First-order transition. Enthalpy and heat capacity of resorcinol.

takes place at constant temperature, producing a discontinuity in the volume-temperature curve. This discontinuity is emphasized in the graph of the coefficient of expansion, *i.e.*, the first derivative of the volume with temperature, which exhibits an infinite value at the change of phase. The same behavior is manifested in practically all primary thermodynamic properties, *e.g.*, the enthalpy and its first derivative, the heat capacity (Fig. 5-14). The change in enthalpy accompanying a change of phase is of considerable industrial as well as theoretical importance and is equivalent to the latent heat (of fusion, vaporization, etc.). Phase changes that are accompanied by such discontinuities in the density, enthalpy, and other primary physical properties are termed *first-order transitions*.

Solids commonly exhibit the property of existing in more than one crystalline form. This phenomenon is called *polymorphism*. The change from one polymorphic form to another is a typical first-order transition. For example, there are five crystalline modifications of ice and six solid forms of camphor, three of which are stable at atmospheric pressure. Table 5-6 contains data from which the existence of the latter may be detected.

TABLE 5-6. FIRST-ORDER TRANSITIONS IN *d*-CAMPHOR

Transition	Temperature, deg C	Volume change, cc/g
Solid III-solid II	-32.0	0.064
Solid II-solid I	87.1	0.00187
Solid I-liquid	177.6	

Atoms and molecules exhibit three types of motion—translation, vibration, and rotation. In crystalline solids the atoms and molecules have fixed *mean* positions in a space-lattice from which they do not depart. However, they vibrate about their mean positions, and the amplitudes of vibration increase with rise in temperature. As is evident in using a set of building blocks, a variety of ordered structures should be possible even with only one type of molecule, so that it is not surprising to find that a single compound may exist in several different crystalline modifications. Each of these forms has its own set of conditions, *i.e.*, temperature and pressure range, within which it is stable.

As the temperature of a solid is raised, eventually the increasing energy content of the molecule results in such a large amplitude of vibration that the crystal structure breaks down and a liquid forms within which the molecules move (translate) as well as vibrate. A 10 per cent increase in volume occurs during the melting of most nonmetals. Since x-ray diffraction shows the distance between the molecules to remain about the same, it follows that melting produces holes as well as disorganization in the system. There are many indications that there are crystal nuclei in the liquid, the number and size decreasing as the temperature is raised above the melting-point.

By virtue of their organized structures, crystalline substances may exhibit different properties along different axes. This phenomenon is termed *anisotropism* and is manifested in optical double refraction and variation in the index of refraction, coefficient of linear expansion, etc., with crystal axis. On the other hand, substances of which the atoms or molecules are not arranged in organized patterns, either because of their mode of formation (glasses, amorphous sulphur) or because of continual

translational motion (liquids, gases), exhibit properties which are uniform in all directions. These substances are isotropic. (Cubic crystals are sometimes termed isotropic because most of the properties are the same in all directions; nevertheless, as the x-ray pattern indicates, they are crystalline.) Whether a solid is anisotropic is not always a simple matter to establish. For this purpose, x-ray examination is of such widespread applicability that it can very well be made the basis for the definition of anisotropism. By this token, any substance giving a distinct x-ray diffraction pattern would be termed *anisotropic*.

Since there can be no gradual transition from one type of *order* to another, an anisotropic substance should always exhibit abrupt transition points. This is found to be true from all studies of changes of state involving an anisotropic substance, whether it be melting to a liquid or changing from one anisotropic form to another. On the other hand, there can be but one kind of *disorder*, or lack of arrangement. Therefore it should be experimentally possible to change continuously from one isotropic form to another, *e.g.*, from liquid to gas. Such a change can, in fact, be achieved around the critical temperature. Similarly, a solid glass melts gradually to a mobile liquid since both forms are isotropic.

From the above it is obvious also why a liquid can be supercooled, whereas a solid cannot exist above its melting point. Arrangement into a definite space-lattice requires a certain precise juxtaposition of atoms or molecules. This arrangement may take time, whereas the state of disorder obviously can be instantly achieved once thermal agitation is sufficient to break the bonds of attraction. For the same reason a solid can be heated above a transition point at which another anisotropic form should set in and can also be cooled below a transition point; *i.e.*, owing to the restricted character of the atomic and molecular motions in a crystal, the velocity of transition among anisotropic forms is very low, and the various forms can be kept for long periods of time under conditions at which they are metastable.

Thus far we have said little about rotational motion. While all molecules in the gaseous and liquid states rotate, this motion is much less common in solids. Therefore, for most substances the inception of rotation coincides with melting. However, many spherical molecules, such as CCl_4 , and flat molecules with symmetry about a single axis, such as benzene compounds, exhibit rotation in a crystalline solid state. In these substances the inception of rotation often results in a first-order solid-solid transition.

One of the methods of detecting the inception of rotation is by dielectric-constant measurements. As pointed out in Chap. 2, the dielectric constant is a measure of the presence of polar groups. To be active, the

polar groups must be able to align themselves with the applied electric field. In the liquid state such alignment is readily effected since the molecules and polar groups are free to rotate. In the solid state, on the other hand, rotational motion is usually restricted, and orientation in an imposed field is more difficult. As a consequence, the dielectric constant of the solid is generally lower than that of the liquid. Thus, the dielectric constant of nitromethane drops from 44 to 3.5 at the freezing point, the dielectric constant of water is 81, and that of ice is about 3. (The value of 3 or less is characteristic both of nonpolar molecules and non-

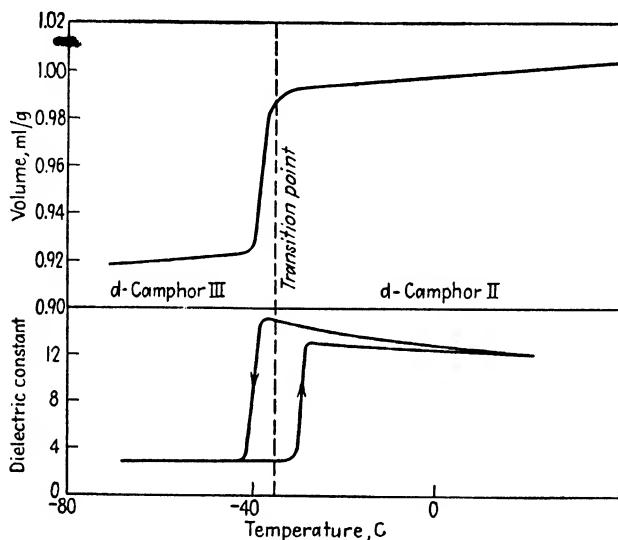


FIG. 5-15. First-order transition. Specific volume and dielectric constant of *d*-camphor. [A. H. White and S. O. Morgan, *J. Am. Chem. Soc.*, **57**, 2078 (1935).]

rotating polar molecules.) However, it is obvious that even in the solid state an orientation of polar structures could take place if the latter structures were able to rotate. If, therefore, a *solid* exhibits a sharp decrease in dielectric constant at a particular temperature, this must indicate a decreased ability of its polar structures to rotate.

Figure 5-15 is a record of the temperature dependence of the specific volume and dielectric constant of *d*-camphor. Evidently at around -32°C the inception of rotation of the molecules causes a first-order transition from solid III to solid II (Table 5-6). This transition is accompanied by a distinct change in crystal form. (As is common with dielectric constant and many other properties that change at a transition point, there is a hysteresis effect, so that the curve for rising temperature does not coincide with that for falling temperature; hence the loop in Fig. 5-15.)

In previous paragraphs it was pointed out that, for most substances, rotation first manifests itself at the melting point but that, for highly symmetrical or planar molecules, rotation often begins at temperatures below the melting point and is responsible for transitions occurring while the substance is still in the solid state. It also happens that these symmetrical molecules are generally characterized by a melting point which is high for their kind and by a short temperature range of existence in the liquid state. It will now be indicated why this correlation of properties exists.

The inception of rotation while the substance is still in the solid state must tend to increase the melting point. This is best seen by application of Eq. (2-5) as follows: At the melting point, solid and liquid are in equilibrium so that $\Delta G = 0$ and

$$T_f = \frac{\Delta H}{\Delta S} = \frac{H_d - H_c}{S_d - S_c} \quad (5-7)$$

where T_f is the melting point and H_d , H_c , S_d , and S_c are the enthalpies and entropies of the disordered (liquid) and crystalline (ordered) states, respectively. Now then, if rotation starts at a transition while the material is still in the solid state, much of the entropy increase that would normally occur at the melting point takes place instead at the solid-solid transition in question. As a result, the entropy increase left for fusion [ΔS of Eq. (5-7)] is small, and the melting point is consequently high.

This very important point is aptly illustrated by consideration of the two isomeric hydrocarbons listed in Table 5-7. The difference between

TABLE 5-7. EFFECT OF MOLECULAR ROTATION IN SOLID ON MELTING POINT

Compound	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3 - \text{C} - \text{CH}_2 - \text{CH}_2 - \text{CH}_3 \\ \\ \text{CH}_3 \end{array}$	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3 - \text{C} - \text{CH} - \text{CH}_3 \\ \quad \\ \text{H}_3\text{C} \quad \text{CH}_3 \end{array}$
Boiling point	79 C	81 C
Solid-solid transition point	None	-152 C
ΔS_{trans}		4.7
Melting point	-125 C	-25 C
ΔS_f	9.5	2.1
Range of existence in the liquid state	204 C	106 C

them is solely a matter of shape, the second being nearly spherical. Since they are identical in molecular weight and chemical constitution, it is not surprising that their boiling points are almost identical. But while the first exhibits no solid-solid transition, the second does; and, in keeping with the previous discussion, the entropy of fusion of the second

is small and its melting point high for its kind. Finally, while the first exists as a liquid over a range of 204° , the corresponding range for the second is only 106° .

514. The Nature of Second-order Transitions. Until about 1925, the only transitions recognized in pure crystalline solids were of the polymorphic kind, *i.e.*, inversion from one crystalline modification to another. As already indicated, inversions of this type are first-order transitions and are characterized by a distinct change in the crystal lattice, each modification having well-defined physical properties that alter by discontinuous steps at a transition point where two neighboring modifications are presumably in equilibrium. In 1930, the possibility of another type of transition was first suggested, and evidence for its existence was soon found, notably from dielectric-constant measurements on hydrogen chloride and other molecules of small moment of inertia.

When ammonium chloride or sodium nitrate is heated, the heat capacity and volume relations undergo gradual but anomalous changes, which reach a maximum at a particular temperature. No profound alteration of the crystal lattice accompanies these changes. Nevertheless, a transition is indicated. This behavior is satisfactorily accounted for by assuming that in the transition range one of the ions, *e.g.*, NH_4^+ or NO_3^- , begins to rotate while still maintaining its mean position in the space-lattice. Such changes are termed *second-order transitions*, a typical case being shown in Fig. 5-16. Unlike a first-order transition, the primary physical properties of both forms of the substance are the same at a second-order transition point. However, the temperature dependence of these properties undergoes a change in direction. Consequently, the first derivative properties like heat capacity and expansion coefficient change discontinuously. Figure 5-16 should be compared with Fig. 5-14. The changes occurring at second-order transitions are much less marked than those accompanying the first-order type, which is one of the reasons for the considerably smaller number that have been detected. Another reason is that in most low-molecular-weight substances the inception of rotation also causes a first-order transition, usually melting. Borderline cases also exist—a slight increase in volume owing to rotation but no x-ray evidence of change in lattice structure.

Second-order transitions have been found in many of the paraffins and their derivatives, where x-ray studies reveal that during the transition the cross section of the molecules changes from an elliptical to a circular form. This is the change to be expected if rigidly bound hydrocarbon chains become free to rotate about their long axes.

In harmony with the theory that the space-lattice remains unaltered, no superheating or supercooling lags have been detected in second-order transitions of low-molecular-weight substances.

The absence of an enthalpy change in second-order transitions indicates the absence, also, of an entropy change. Instead, the entropy increase occurs over the temperature range below the transition point, in which range the heat capacity is abnormally high.

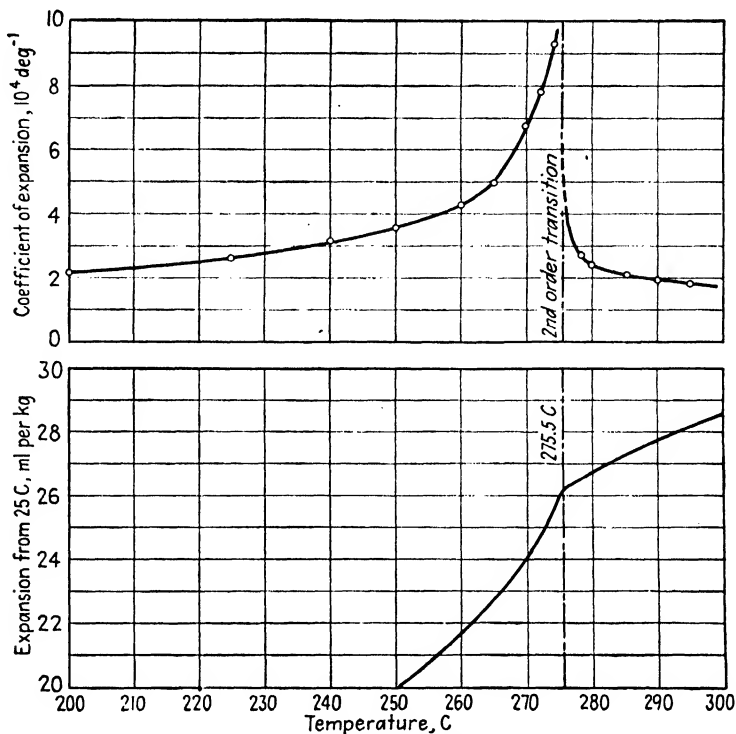


FIG. 5-16. Second-order transition. Thermal expansion of sodium nitrate. [P. C. Kracek, *J. Am. Chem. Soc.*, **53**, 2609 (1931).]

515. Transition Phenomena in High Polymers. Organic high polymers exhibit a variety of changes in state that affect their physical and mechanical properties. Temperature and external stress are the principal determinants of these transitions. In many cases, time is an important additional factor. Apparently, the average high-polymer solid contains several states of order simultaneously, never being all ordered or entirely disordered, and these states change slowly but more or less continuously under the influence of temperature and external stress.

516. First-order Transitions. Some high polymers possess such geometrical regularity that they crystallize sufficiently to manifest an experimentally observable solid-liquid transition (Table 5-8). On heating polyvinylidene chloride above its softening point and cooling quickly, the product is soft, weak, and pliable and has the x-ray diffraction pattern

of an amorphous material. If it is held at room temperature without further treatment, it gradually hardens while crystallizing with a random crystal arrangement, as shown by a pronounced powder diagram (Fig. 5-7a). Not only are the crystallization phenomena every bit as definite as with a low-molecular-weight compound, but the rate of crystallization at room temperature is considerably greater than that of amorphous sulfur, a significant comparison because the melting points of polyvinylidene chloride and sulfur are similar. In a few cases, high polymers melt sharply. For example, in polyhexamethylene sebacamide (polyamide 6-10), the solid-liquid transition occurs over a 2° interval under equilibrium conditions with little hysteresis. In most cases however, there is considerable hysteresis, which is not surprising in view of the lengths of the molecules and their consequent low mobility and hampered motions.

TABLE 5-8. FIRST-ORDER TRANSITION (TRUE MELTING POINTS) OF HIGH POLYMERS (Melting points of some polyesters given in Table 1-2)

Polymer	Highest First-order Transition Temperature of Unstressed Substance, Deg C
Hevea rubber.....	About 25
Chloroprene.....	About 30
β -Gutta-percha.....	56
α -Gutta-percha.....	65
Thiokol A.....	About 70
Polyethylene....	115
Polyvinylidene chloride.....	185
Cellulose tributyrate.....	185
Polyamide 10-10.....	194
Polyamide 6-10.....	209
Cellulose tripropionate.....	225
Polyamide 10-6.....	230
Polyamide 6-6.....	250
Polyamide 4-6.....	278
Cellulose triacetate.....	302
Polytetrafluoroethylene.....	327

Data from several sources, notably

COFFMAN, D. D., *et al.*, *J. Polymer Sci.*, **3**, 306 (1947).

MALM, C. J., C. R. FORDYCE, and H. A. TANNER, *Ind. Eng. Chem.*, **34**, 430 (1942).

WOOD, L. A., in "Advances in Colloid Science," Vol. 2, MARK and WHITBY, editors, Interscience Publishers, Inc., New York, 1946.

Polyvinylidene chloride and all other high polymers exhibiting such first-order transitions differ in one significant respect from low-molecular-weight substances, *viz.*, during the first-order transition the material may become transparent and softer, but it by no means turns into a mobile liquid. In some cases the substance becomes a very viscous liquid, and in other cases it becomes a rubber. That high polymers do not melt to mobile liquids may be explained as follows (see also Sec. 321).

Monomeric vinylidene chloride is a volatile, mobile liquid at room temperature. Each molecule vibrates about a mean center; but as in all typical liquids this center is not fixed, and the particles undergo translational Brownian movement and change places with respect to one another frequently, *i.e.*, self-diffusion is rapid. This lack of fixity accounts for flow and inability to maintain definite shape and dimension under stress.

In polyvinylidene chloride above the melting point, each individual mer in a chain vibrates about a mean center, as does a monomer molecule in liquid monomer, and furthermore undergoes similar short-range Brownian movement. However, since it is part of a very long chain molecule, it is not able to diffuse very far from its original position unless it can drag along with it the entire chain. Any such displacement of chains as a whole is impeded by their long-range interaction and entanglement and is consequently very infrequent in the absence of external stress. This means that self-diffusion and flow are highly restricted in spite of the high local mobility at any one point. In other words, in a mass of high-polymer chains two Brownian movements rather than one must be considered, the motion of the individual mers and the motion of the chain as a whole. These have been termed the *internal* or *micro-Brownian* and the *external* or *macro-Brownian movements*, respectively.

In a typical rubber, the internal Brownian motions at room temperature are considerable, imparting a high local mobility, or "liquidity," which permits rapid and extensive stretching and retraction on the application and release of tensile stress, but long-range interaction and entanglement still prevent self-diffusion and enable the mass to maintain its shape and to deform elastically under moderate stresses not too long maintained. This concept of a rubber as what might be called a *captive liquid* is of fundamental importance.

The value of the first-order transition is influenced by the factors of polarity, symmetry, and orientation, as previously described in Chap. 2. For example, characteristic high-polymeric strength and toughness are attained by polyethylene at one-tenth the average molecular weight of

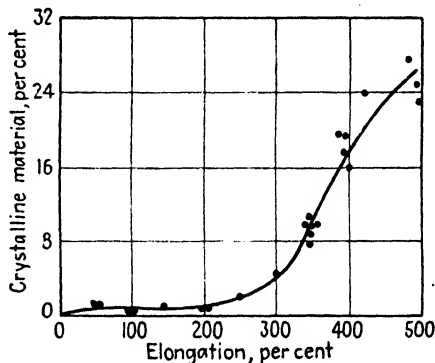


FIG. 5-17. Crystallization of stretched Hevea rubber at 20 C. [A. J. Wildschut, *J. Applied Phys.*, 17, 51 (1946).]

polystyrene, despite the considerably greater molar cohesion of the latter. This phenomenon is due to the efficient molecular packing (crystallization) of polyethylene, as compared with polystyrene. The latter has such poor molecular symmetry that it exhibits no first-order transition and no orientation effects are observed when it is stretched.

(a)

(b)

(c)

(d)

FIG. 5-18. X-ray diffraction patterns of rubbers. (a) Hevea rubber, unstretched. (b) Hevea rubber, 500% elongation. (c) Buta S, unstretched. (d) Buta S, 500% elongation. [(a) and (b) *S. D. Gehman, Chem. Revs.*, **26**, 203 (1940). (c) and (d) *R. E. Morris and C. B. Jordan, Rubber Age (N. Y.)*, **55**, 161 (1944).]

Stress-induced orientation of high polymers has already been described (Secs. 231 and 232). In many cases the structure becomes sufficiently ordered to exhibit crystallinity as evidenced by the appearance of an x-ray fiber pattern. An especially interesting case is that of polyisobutylene, which is always amorphous when unstretched and on stretching gives one of the most beautiful fiber patterns known to x-ray analysis

(Fig. 5-29b). Its crystallization is a completely reversible phenomenon. On release of the tensile stress the sample contracts immediately and spontaneously, and the x-ray pattern reverts to the amorphous type.

The first-order transition of natural rubber was one of the earliest discovered in high polymers. Hevea rubber exhibits both spontaneous crystallization in the unstretched form and stress-induced crystallization. The extent of crystallization is a function of the amount of elongation (Fig. 5-17).

At room temperature, the common form of unstretched rubber is amorphous (Fig. 5-18a). Below room temperature, crystallization results, and the product, frozen rubber, yields a typical powder pattern (Fig. 5-19), showing that crystallites have formed and are randomly arranged. The rate of crystallization increases as the temperature falls below 15 C, reaches a maximum at -25 C, and then decreases below this temperature, ceasing altogether at -50 C. At -25 C the "half time" for crystallization is 2 to 3 hr. (These rate phenomena of supercooling and crystallization are not peculiar to high polymers. Identical effects are observed with low-molecular-weight substances. Below a minimum temperature the molecules are so thoroughly immobilized that they cannot arrange themselves into crystal lattices.)

The enthalpy and volume changes of natural rubber at its melting point are the same as those of typical low-molecular-weight substances (Fig. 5-20). Its low rate of crystallization permits great supercooling so that the properties of amorphous rubber may be determined to very low temperatures.

As with low-molecular-weight materials, the transition temperatures of high polymers are functions of the external pressure. In the case of Hevea rubber, the transition temperature is raised by pressure, increasing approximately 30 C under a pressure of 1,000 atm.

Similarly, tensile stress raises the transition temperature. Historically, the crystallization of natural rubber by tension (Fig. 5-18b) was discovered before its spontaneous crystallization at low temperatures. The phase diagram for tensile stress is known only approximately

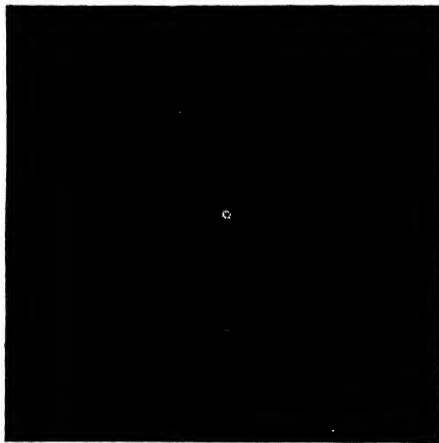


FIG. 5-19. X-ray diffraction pattern of frozen unstretched Hevea rubber. [S. D. Gehman, *Chem. Revs.*, **26**, 203 (1940).]

(Fig. 5-21). The crystallization of rubber by tension shows little hysteresis, except near the boundary curve. Thus, at 25 C and elongations between 150 and 500 per cent, crystallization continues for many hours after stretching, while, beyond 500 per cent elongation, what crystallization occurs takes place immediately.

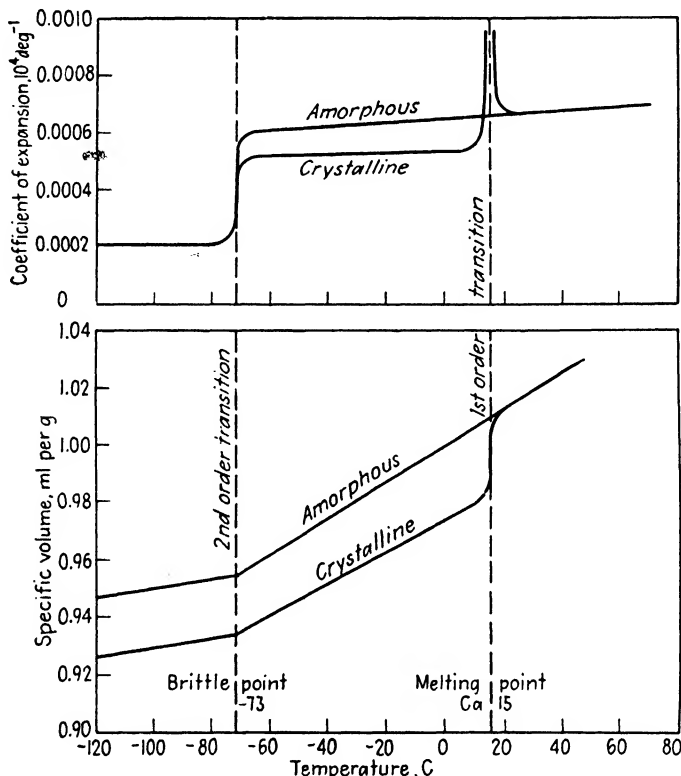


FIG. 5-20. Volume-temperature relations of Hevea rubber. [N. Bekkedahl, *J. Research Natl. Bur. Standards*, **13**, 411 (1934).]

Crystalline regions in rubber, whether produced by stress or low temperature, act like particles of a reinforcing filler in stiffening the rubber. The term *frozen rubber* is an indication of its relatively hard and nonelastic character. The term *stark rubber* is used for frozen rubber with a melting range extending above 25 C.

The melting of frozen rubber exhibits several unique features (Fig. 5-22):

1. A particular batch of crystals begins to melt at a temperature about 5 C above that at which it was formed.

2. Melting occurs over a range of temperatures, not sharply at a fixed temperature.

3. The range of melting is a function of the temperature at which crystallization occurred.

4. The melting range is not a function of the degree of crystallization since partly crystallized rubber melts over the same range as does rubber in which crystallization is more complete. Similarly, it is not a function of molecular weight or degree of vulcanization.

These effects are peculiar to high polymers. The first two are not surprising in view of the low heat of fusion of high polymers, the small difference in entropy between crystal and liquid, and their structures, which produce high relaxation times and hinder crystallization. However, the last two have not yet been satisfactorily explained.

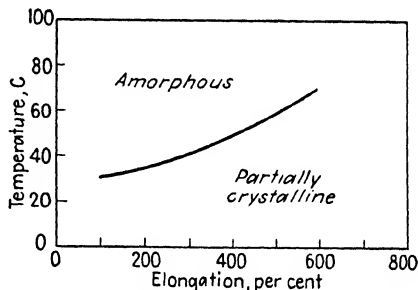


FIG. 5-21. Effect of tensile stress and temperature on the crystallization of Hevea rubber. Line represents approximate conditions for inception of crystallization. Extent of crystallization at constant temperature increases with elongation (See Fig. 5-17).

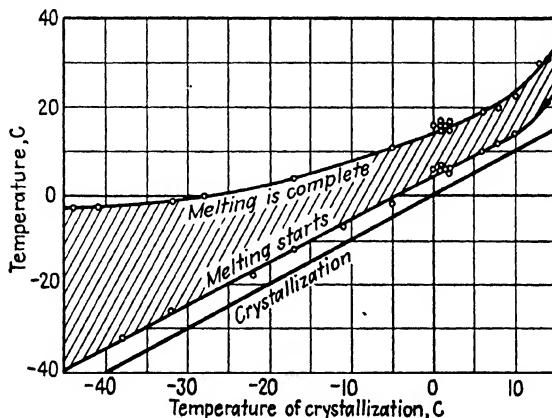


FIG. 5-22. Melting range of Hevea rubber. A vertical line passes through the melting range corresponding to a particular temperature of crystallization. (L. A. Wood in "Advances in Colloid Science," Vol. 2, Mark and Whitty, editors, Interscience Publishers, Inc., New York, 1946.)

517. Second-order Transitions. Measurements of the properties of both crystalline and amorphous unvulcanized Hevea rubber at low temperatures indicate the existence of a transition at -73°C that involves no latent heat. This and other properties indicate it is second-order (Fig.

5-20). Such a transition occurs at other fairly well defined and characteristic temperatures in the case of all high-polymeric materials that have been studied (Table 5-9). That is, in direct contrast with low-molecular-weight substances, a second-order transition is universal with high polymers, whereas a first-order transition (true melting point) is frequently absent. The explanation for this state of affairs is relatively simple.

TABLE 5-9 SECOND-ORDER TRANSITIONS OF HIGH POLYMERS
(Values for unstressed substances with little or no plasticizer)

Polymer	Second-order Transition Temperature, Deg C
Polybutadiene.....	-85
Polyisobutylene.....	-74
Hevea rubber.....	-73
Polyethylene.....	-68
Polyvinylidene chloride.....	-17
Polymethyl acrylate.....	3
Polyvinyl acetate.....	28
Ethyl cellulose.....	43
Polyamide 6-6.....	47
Polymethyl methacrylate.....	60
Cellulose nitrate.....	66
Cellulose acetate.....	69
Polyvinyl chloride.....	75
Phenol-aldehyde thermoset.....	C'a. 75
Polystyrene.....	81
Glycerol-phthalic anhydride resin.....	C'a. 85

Data from several sources, notably

BOYER, R. F., and R. S. SPENCER, in "Advances in Colloid Science," Vol. 2, MARK and WHITBY, editors, Interscience Publishers, Inc., New York, 1946.

Consider a liquid high polymer at a temperature sufficiently high to provide extensive micro-Brownian movement—rotational, vibrational, and limited translational. On cooling, the average kinetic energy in each degree of freedom decreases. Owing to the decrease in translational energy, mobility decreases. When the energy of vibration has fallen to the order of the molar cohesion, crystallization takes place, provided that recurrence-symmetry requirements are met. However, such requirements are met by relatively few high polymers. A minor amount of copolymerization (or plasticizer) will lower the crystallization temperature, and an appreciable amount may prevent crystallization entirely. If crystallization does not take place, translation and vibration continue to decrease with fall in temperature and the mobility of the system decreases continuously, the material increasing in hardness and rigidity.

In any case, as the temperature falls, whether crystallization sets in or not, the energy of rotation also falls and eventually reaches the minimum

value necessary to maintain rotation in the particular molecular configuration. Below this temperature, rotation ceases, and this temperature is the second-order transition point. Because rotation is on a micro-molecular scale, symmetry is of no consequence. Therefore all high polymers must have a second-order transition point, whether or not they have a first-order transition point.

As with low-molecular-weight compounds (Table 5-7), as a consequence of the low-temperature rotational transition, highly symmetrical polymeric molecules are characterized by high melting points. The insolubility of simple polymers without hydrogen bonding such as

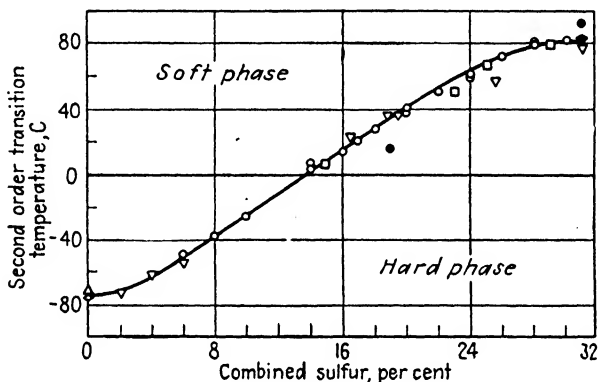


FIG. 5-23. Effect of combined sulfur content on second-order transition temperature of Hevea rubber. (R. F. Boyer and R. S. Spencer in "Advances in Colloid Science," Vol. 2, Mark and Whitby, editors, Interscience Publishers, Inc., New York, 1946.)

polyethylene and polytetrafluoroethylene is likewise the result of the gain of sufficient rotational entropy to make dissolution thermodynamically unattractive.

Although the second-order transition point in high polymers is the temperature at which rotation sets in, it is hardly conceivable that an entire high-polymer molecule could rotate as a unit. The greater probability is that segments of the polymer rotate.

The second-order transition temperature is affected by external pressure or tension, by plasticizer (Fig. 3-4), by copolymerization, by molecular weight, and by still other variables. Figure 5-23 shows the influence of combined sulfur on the second-order transition temperature of Hevea rubber over the entire composition range from unvulcanized rubber to hard rubber. Evidently crosslinking inhibits the freedom of the segments to rotate so that a higher temperature is needed for rotation to begin. Copolymers have second-order transition temperatures between those of the individual pure polymers, but the curve is not linear. Plasticization reduces the second-order transition temperature. Con-

trary to the case with low-molecular-weight substances, time effects are often present, which is obviously due to the much higher relaxation times of the high polymers.

518. *The Rubbery and Glasslike States.* The transition effects in high polymers throw light on the differences between plastics and rubbers. Rubberlike properties are encountered only among high polymers. These properties are so unique as to entitle them to recognition as a special state of matter—the rubbery state.

The absence of rubbery properties in frozen rubber indicates that the rubbery state is amorphous. Furthermore, the spontaneous retraction of stretched rubber with the concomitant melting of the crystallites formed on stretching indicates that the amorphous state is the stable one. (In this respect, rubbers differ from low-molecular-weight materials like sulfur and quartz, which can exist in the amorphous condition. In these materials the amorphous form can be attained only by rapid supercooling of the liquid. However, in time, within a temperature range allowing sufficient mobility, the metastable amorphous solid form reverts spontaneously, although perhaps very slowly, to the stable crystalline form. The devitrification of glass is a well-known illustration.)

As stated previously, the crystallization of Hevea rubber occurs very slowly, and thus there is little difficulty in maintaining the amorphous state at low temperatures. Below -50°C the rate of crystallization is substantially zero, and rubber has been kept amorphous down to -259°C . Nevertheless, the rubbery properties disappear completely at -73°C , the second-order transition temperature, despite the fact that the material remains amorphous. This indicates that rotation of the chain segments is necessary to give the system sufficient freedom to allow extension and retraction. Below the second-order transition temperature, rubbers are brittle and cannot be bent without fracturing.

The basic criteria for the rubbery state are therefore that (1) the material must be a high polymer; (2) it must be above its second-order transition temperature; (3) it must be in the amorphous state. These criteria must be met at room temperature for a material to be designated a rubber in the common sense of the word. Thus, polystyrene meets all the conditions above its second-order transition point, 81°C , where it acquires rubbery properties. Nevertheless, it is known as a plastic.

Evidently the second-order transition temperature is an important determinant of whether a high polymer is a rubber or a plastic. External plasticization increases softness, etc., of a plastic, as described in Sec. 318. If sufficiently plasticized to lower the second-order transition temperature to below room temperature, somewhat rubberlike properties may be conferred on the product.

When Hevea rubber is drastically stretched at room temperature, so much molecular alignment and crystallization result that the stretched state assumes properties typical of a fiber (*e.g.*, a tensile strength of about 26,000 psi on the basis of actual cross section at break). For the sake of emphasis, it is well to reiterate that, depending on temperature and manipulation, Hevea rubber can exist as a rubber, a fiber, or a plastic.

Glasslike low-molecular-weight substances comprise an important group of materials. In the broad sense they possess the outstanding physical properties of common glass, such as brittleness, without regard to transparency. Such items as rosin and various other natural resins, stiff pitches, and hard sugar candies are included. Their common characteristics are that they are supercooled amorphous materials composed of relatively small molecules and are brittle and frangible. Below their second-order transition points, high polymers greatly resemble these glasslike materials in physical behavior except that the former are distinctly less brittle. The only essential difference between the two kinds of materials is the size of the molecules. The lower degree of brittleness among the high polymers is no doubt attributable to the flexibility and long-range interaction and entanglement of the molecules or their greater ability to absorb energy.

An approximate phase diagram for high polymers is given in Fig. 5-24*a*. Such a diagram applies for Hevea rubber when the crystalline phase is allowed to form. A similar diagram applies for polyethylene and polyvinylidene chloride, except that the rubbery state is absent or of short range. If the crystalline state does not form, which is the case for most commercial plastic and rubber products, Fig. 5-24*b* represents the phase diagram. Again in many cases the rubbery state is absent or of short range.

519. The Brittle Point. As the temperature of a rubber is lowered, the rubberlike properties are gradually lost, the material hardens, and finally a point is reached at which the sample is brittle and shatters upon the sudden application of load. The temperature at which such breakage takes place is known as the *brittle point* and is of great practical importance because it represents the lower limit of the useful temperature range of the material.

It has been customary to identify this brittle temperature with the second-order transition temperature, and for commercial polymers of high molecular weight the two temperatures are close. However, there are several fundamental differences between the two temperatures, which become very apparent for polymers of low molecular weight.

First of all, the brittle-point test is empirical, so that the numerical values vary with the method of test, the rate of loading, the thickness of

the sample, etc. That is, the brittle temperature is that temperature at which the time interval required by the sample to undergo the necessary deformation is just equal to the time interval over which the load is applied

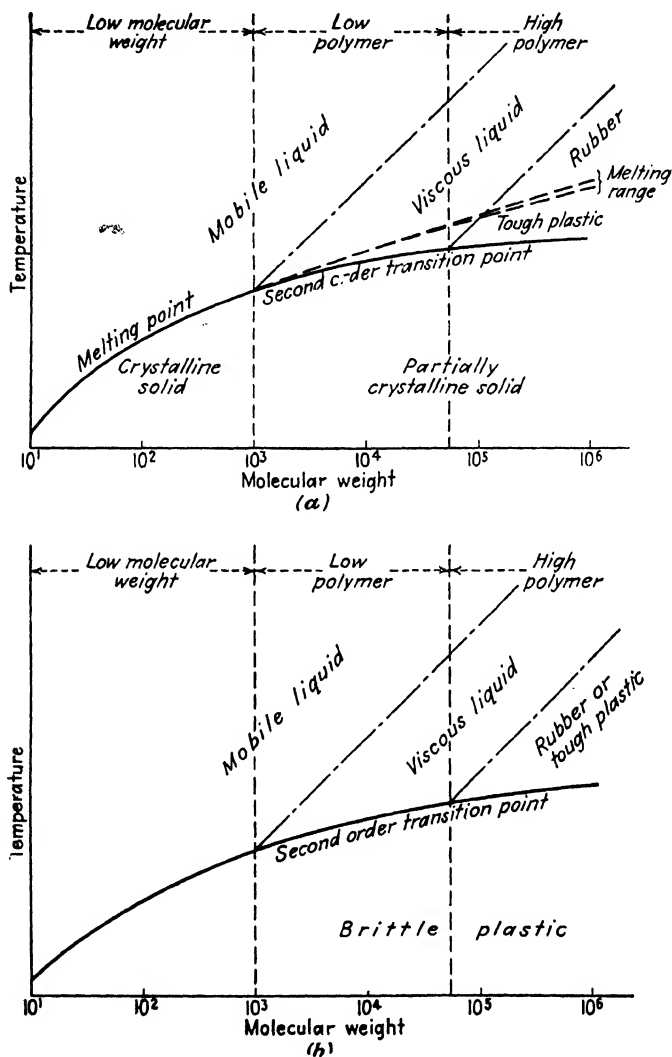


FIG. 5-24. Schematic phase diagrams. (a) High-polymer crystalline phase forms. (b) No high-polymer crystalline phase forms.

in the test method. Above this temperature the time is more than sufficient, and the sample deforms without breaking; at lower temperatures the sample cannot deform rapidly enough, and it breaks. Obviously,

the lower the molecular weight, the less the long-range interaction and entanglement, and the higher the brittle point (Fig. 5-25). Addition of plasticizer decreases relaxation time and thus lowers the brittle temperature (Fig. 3-4, page 83).

The second-order transition is determined by thermal-expansion or heat-capacity studies. Both these are low-rate tests, so that the deformation of the sample is not a factor. The second-order transition temperature is that temperature at which the molecular segments have

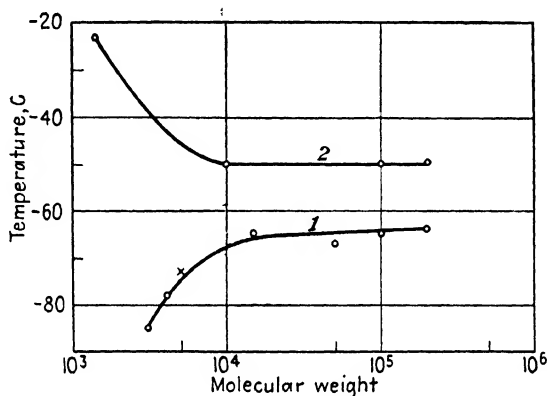


FIG. 5-25. Effect of molecular weight on transition point (Curve 1) and brittle point (Curve 2) of polyisobutylene. (R. F. Boyer and R. S. Spencer in "Advances in Colloid Science," Vol. 2, Mark and Whitby, editors, Interscience Publishers, Inc., New York, 1946.)

acquired sufficient energy to overcome local cohesion and restraint and have begun to rotate. The inception of rotation obviously should and does decrease brittleness greatly, so that the qualitative correlation of brittle-point and second-order transition temperature is to be expected. However, the quite different methods of test will obviously produce quantitative differences in the numerical values. The second-order transition temperature depends upon the relaxation times of the molecular segments, while the brittle-point temperature depends upon these relaxation times and those of the sample as a whole. The differences between the two tests become exaggerated with low polymers. The lower the molecular weight, the less the molecular restraints and the lower the second-order transition temperature (Fig. 5-25), the effect being just opposite to that on the brittle point.

STRUCTURES OF SILICATES AND SILICONES

520. For many years the great variety of the silicates, their supposed complexity, and their apparently anomalous formulas, which did not seem to be governed by the usual simple valence rules, presented a complicated puzzle to chemists and mineralogists. One of the greatest achievements

of x-ray analysis has been the elucidation of the silicate structures, mainly through the contributions of W. L. Bragg and L. Pauling. Once their basic structure has been revealed, order follows chaos, and the silicates fall logically into a simple classification that accounts not only for their

chemical formulas but also for their physical and mechanical properties.

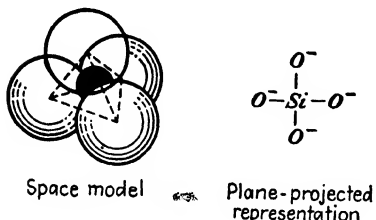


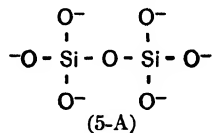
FIG. 5-26. The silicon tetroxide ion, $(\text{SiO}_4)^{4-}$.

The fundamental structural unit of the silicates is the orthosilicate ion, a regular tetrahedron with the smaller silicon atom symmetrically surrounded by four of the larger oxygen atoms as shown in Fig. 5-26. In this orthosilicate ion, $(\text{SiO}_4)^{4-}$, the ratio of silicon to oxygen is 1:4. The

orthosilicates themselves are saltlike compounds with individual tetrahedra associated with various metal ions as in olivine, Mg_2SiO_4 , and zircon, ZrSiO_4 . The crystals of these compounds have typical ionic lattices.

One of the minor complications in silicate structures is the isomorphous replacement of cations by others with the same aggregate charge, as in garnet, $\text{Ca}_3\text{Al}_2(\text{SiO}_4)_3$. A more serious complication is the appearance of nonmetallic atoms in the cation, as in topaz, $(\text{AlF})_2\text{SiO}_4$. The latter phenomenon was one of the stumbling blocks in the earlier efforts to represent silicates in harmony with ordinary valence rules, especially when oxygen or hydroxyl appeared in the cation, as in cyanite, $(\text{Al}_2\text{O})\text{SiO}_4$.

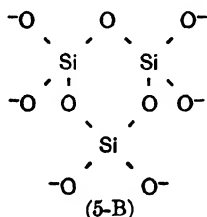
In high-polymer parlance, the orthosilicate tetrahedron is potentially polyfunctional, and hence polymers of all types are possible. Indeed, the bewildering number of silicates that have been identified is traceable in part to the fact that two or more $(\text{SiO}_4)^{4-}$ tetrahedra may "react" by sharing oxygen atoms with one another. The first step is the formation of the orthodisilicate ion, $(\text{Si}_2\text{O}_7)^{6-}$, which results from the sharing of one oxygen by two tetrahedra.



Typical examples of this type of silicate are melilite, $\text{Ca}_2\text{MgSi}_2\text{O}_7$, and hemimorphite, $[\text{Zn}_4(\text{OH})_2]\text{Si}_2\text{O}_7 \cdot \text{H}_2\text{O}$. In these compounds the ratio is $\text{Si}:\text{O} = 1:3.5$.

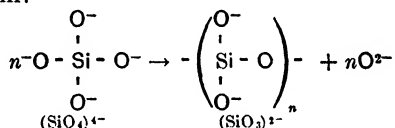
If three tetrahedra share two oxygens with one another, the resulting structure may be either linear or cyclic. The former is similar to the

orthosilicate but longer. It has the formula $(\text{Si}_3\text{O}_{10})^{8-}$ with a ratio of $\text{Si}:\text{O} = 1:3.33$. The latter, on the other hand, has been shown by x-ray analysis to have structure (5-B).



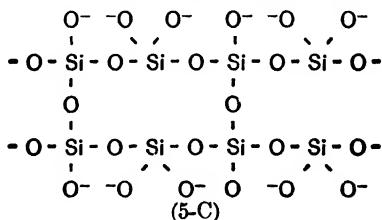
Hence the formula is $(\text{Si}_3\text{O}_9)^{6-}$, and the ratio is $\text{Si}:\text{O} = 1:3$. An example is benitoite, $\text{BaTiSi}_3\text{O}_9$. In the important mineral beryl, rings of twice this size exist as $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$.

Extensive "polymerization" of $(\text{SiO}_4)^{4-}$ tetrahedra via the bifunctional mechanism outlined above evidently takes place in some silicates, yielding high-polymer chains. This polymerization may be represented by the following equation, although this is probably not the actual reaction mechanism:



These chain polymers are called *pyroxenes*, a typical example being diopside, $[\text{CaMg}(\text{SiO}_3)_2]_n$. The ratio is $\text{Si}:\text{O} = 1:3$.

In the more important *amphiboles*, cross-linkage has taken place so that double chains have formed. The structure revealed by x-ray diffraction studies is (5-C). Twin-chain polymers such as these have not



yet been produced by synthetic methods. The mer of these double chains is $(\text{Si}_4\text{O}_{11})^{6-}$, and the ratio is $\text{Si}:\text{O} = 1:2.75$. An example is tremolite, $[\text{Ca}_2\text{Mg}_5(\text{OH})_2(\text{Si}_4\text{O}_{11})_2]_n$.

The oxygen ions of the compounds depicted above are joined to metallic ions. The compounds thus formed, whether small molecules or high polymers, are attracted to one another by secondary valence forces. These binding forces are not as strong as the $\text{Si}-\text{O}$ covalent bonds *within*

the compounds. As a consequence the chainlike molecules are readily separable into fibers. The various kinds of asbestos have this structure. Chrysotile, $[(\text{MgOH})_6\text{Si}_4\text{O}_{11}]_n$, is an important example. The high degree of orientation in this natural fiber is revealed by its x-ray fiber diagram (Fig. 5-27).

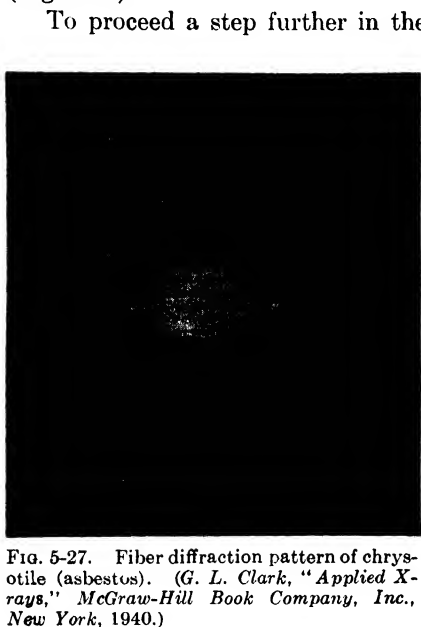
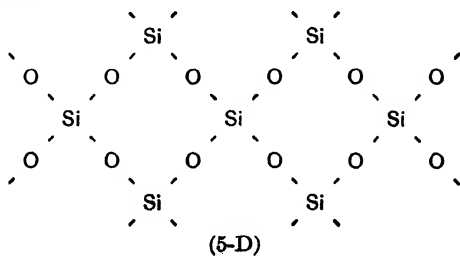


FIG. 5-27. Fiber diffraction pattern of chrysotile (asbestos). (G. L. Clark, "Applied X-rays," McGraw-Hill Book Company, Inc., New York, 1940.)

To proceed a step further in the cross-linking process, if individual silicate chains are cross-linked laterally to one another by still more extensive sharing of oxygens, plane-polymerized sheets or layers are formed. The fundamental unit is $(\text{Si}_2\text{O}_6)^{2-}$, and the ratio is $\text{Si}:\text{O} = 1:2.5$. An example is talc, $[\text{Mg}_3(\text{OH})_2(\text{Si}_2\text{O}_6)_2]_n$, which crystallizes in flakes. The layers are held to one another by secondary valence forces, which are much weaker than the covalent silicon-to-oxygen bonds within the sheets. Hence these materials slide readily over one another or cleave in thin laminations. Micas possess this sort of structure. (Thus far, no well-oriented plane polymers have been produced by synthetic methods.)

If the cross-linking process proceeds still further, three-dimensional space-polymerized silicates result. The ultimate of this process is a structure in which each tetrahedron shares four oxygens, one each with four other tetrahedra. The mer in this case is (SiO_2) , and the various polymorphic forms of silica such as quartz, tridymite, and cristobalite are all space polymers, with the formula $(\text{SiO}_2)_n$ where the ratio is $\text{Si}:\text{O} = 1:2$ [structure (5-D)]. There exist several spatial arrangements in these silicas as evidenced by their different crystal forms, densities, and x-ray patterns.



The silica space-lattice is neutral and therefore cannot accommodate cations. However, another hitherto perplexing complication in silicate structures is the partial replacement of the silicon atom in the anion by other atoms of similar size, notably aluminum and beryllium. The effect of these replacements is best visualized by formally representing the silicon as completely ionized Si^{4+} . Replacements by Al^{3+} or Be^{2+} do not alter the fundamental silicate structure but do result in silicate lattices with enhanced negative charges, which must be offset by the introduction of extra cations elsewhere in the structure. Examples are

1. Fiber polymers. Amphiboles with anion $(\text{Si}_3\text{AlO}_{11})^{7-}$ instead of $(\text{Si}_4\text{O}_{11})^{6-}$
2. Sheet polymers. Micas with anion $(\text{Si}_3\text{AlO}_{10})^{5-}$ instead of $(\text{Si}_2\text{O}_5)_2^{4-}$, as in muscovite, $\text{KAl}_2(\text{OH})_2(\text{Si}_3\text{AlO}_{10})$
3. Space polymers. Feldspars with anion $(\text{AlO}_2)^{1-}$ instead of the uncharged mer (SiO_2) , as in orthoclase, $\text{K}(\text{AlO}_2)(\text{SiO}_2)$

The *zeolites* are space-polymerized silicates of outstanding practical importance. X-ray examination has afforded the clue to their interesting behavior. Some of the silicon ions have been replaced by aluminum ions, and the space-lattice is such that the structure resembles a negatively charged silicate honeycomb with large holes. The extra cations needed to produce electrical neutrality (mainly sodium ions) are distributed in the holes of the network. When hard water is run through this porous structure, the Ca^{2+} and Mg^{2+} ions are more strongly attracted to the silicate network than the sodium ions. Ion exchange results, and the water is softened (Sec. 1615).

The x-ray photographs of glasses show diffuse diffraction bands like liquids. Vitreous silica is apparently composed of crystallites no larger than the unit cell of the crystalline form. Projected on a plane, the structure of vitreous silica (fuzed quartz) is schematically represented by Fig. 5-28*b*. The difference between the crystalline and glassy forms (Figs. 5-28*a* and *b*) is that in the former the SiO_4 groups are arranged regularly, while in the latter they are distributed randomly. In each case the structural unit is the same. The essential similarity results in similar potential energies for the space-lattices, which accounts for the relative stability of the glassy form. The common glasses (Fig. 5-28*c*) have structures similar to vitreous silica except that metallic ionic silicate structures are present. As a result, there is less silicon to oxygen bonding, and the softening temperatures are lower.

It is appropriate at this juncture to consider the silicones, synthetic organosilicon polymers developed in the early 1940's. They are especially important since they are intermediate between organic carbon-based polymers and the inorganic silicon-based silicates and thus can withstand relatively high operating temperatures.

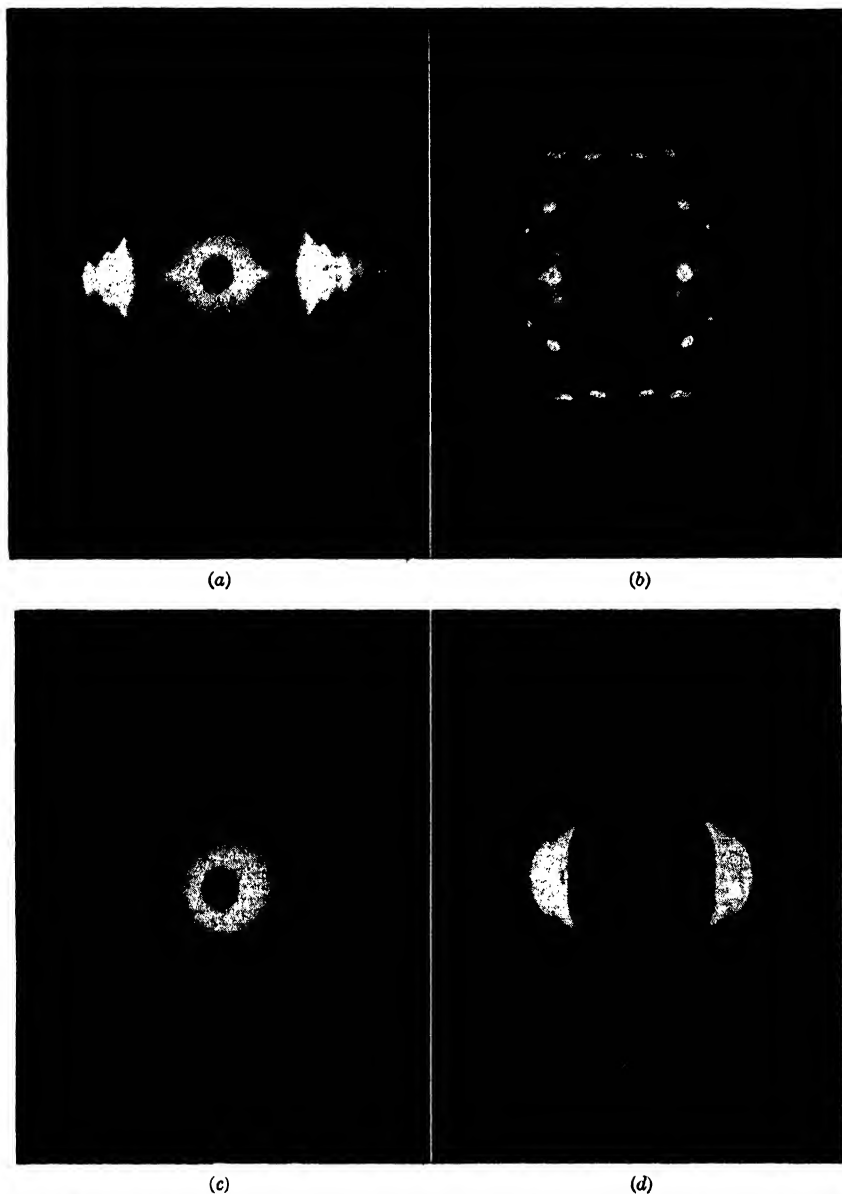


FIG. 5-29. Fiber diffraction patterns of several synthetic high polymers. Fiber axis vertical. (a) Polyethylene. (b) Polyisobutylene. (c) Polyvinyl chloride. (d) Polyhexamethylene adipamide (Nylon 66). (Courtesy of W. O. Baker and N. R. Pape, Bell Telephone Laboratories.)

STRUCTURES OF SYNTHETIC HIGH POLYMERS

521. In low-molecular-weight linear substances the molecules are all of the same length, and, being short, they are often capable of a precise arrangement as in Figs. 5-10a and b. As a consequence, identity periods due to the regularly recurring chain ends appear in the x-ray photograph, and the molecular length (molecular weight) may be deduced from them. Furthermore, the crystals often show definite cleavage planes at the chain ends. In linear-polymeric masses the molecules are not all the same

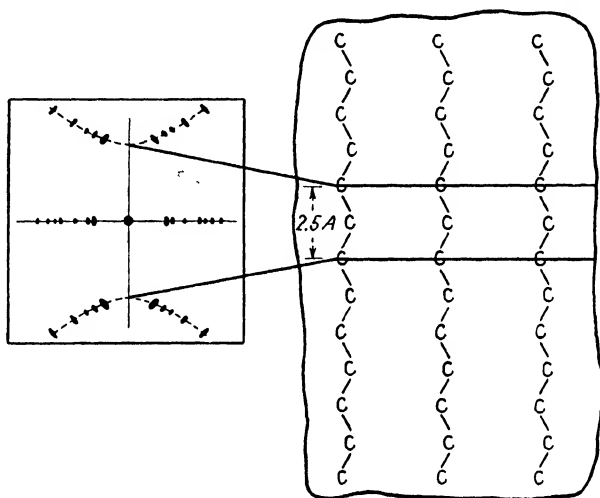


FIG. 5-30. Relation of chain structure in polyethylene to its x-ray fiber pattern. [C. S. Fuller and W. O. Baker, *J. Chem. Education*, **20**, 3 (1943).]

length; and since they are extremely long, perfect alignment throughout the mass never exists. All the evidence indicates that the state of affairs is as represented in Fig. 2-9. Such structures should not show definite cleavage planes. This is borne out in fact. In a crystalline fibrous polymeric mass, therefore, the repeating chemical unit is not the molecule but the mer, and the unit cell is the mer or some simple small multiple of the mer (Table 5-3, page 169).

522. Synthetic Linear High Polymers. Certain synthetic linear polymers offer an excellent basis for study because their chemical compositions are known and they have a high degree of crystallinity yielding sharp x-ray patterns (Fig. 5-29). Furthermore, changes in chemical composition can be correlated with changes in the x-ray patterns.

The simplest organic high polymer is polyethylene. Its fiber pattern is extremely simple, as shown in Fig. 5-29a. Figure 5-30 shows schematically how the layer lines are connected with the fiber period. In this

case, the latter is 2.5 Å, the shortest possible period for an aliphatic chain (Fig. 9-1 and Table 5-3). This indicates that, in the polyethylene crystallite, the molecules lie in the fully extended, planar zigzag form. In polyisobutylene (Table 5-3) an interesting situation exists. If, in the stretched (fibrous) state, the molecules were extended in planar zigzag fashion, the fiber pattern would be similar to that of polyethylene and the fiber period would be 2.5 Å. In fact, however, the x-ray pattern

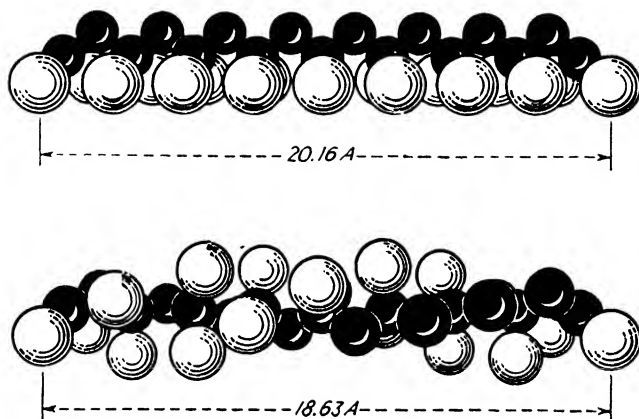


FIG. 5-31. Comparison of probable spiraled form of polyisobutylene chain fiber period (lower) with the configuration it would have in the extended zigzag state (upper). Large spheres are methyl side groups; small spheres are carbon chain atoms. [C. S. Fuller and W. O. Baker, *J. Chem. Education*, **20**, 3 (1943).]

is unusually complicated (Fig. 5-29b), and the fiber period turns out to be 18.6 Å. Evidently the repeating unit contains a considerable number of mers, probably owing to the chain twisting into a helix as in Fig. 5-31. This twisted structure renders close fitting (crystallization) of neighboring chains much more difficult than in polyethylene and helps account for the fact that polyisobutylene is far more rubbery in character. It is interesting to note that, among polyhydrocarbon elastomers, there is a rough correlation between rubberiness and the length of the fiber period.

One may now consider the effects of introducing polar groups along chain molecules at regular intervals. Carothers synthesized such molecules in his polyesters of the types



These molecules are really lengths of paraffin hydrocarbon joined by polar ester linkages. Inasmuch as the C—O bond length is almost that of the C—C bond and the scattering power of the oxygen atom is almost the same as that of the carbon atom, these polyesters may be regarded as

identical with paraffin chains except that at intervals a CH_2 group has been replaced by a $\text{C}=\text{O}$ group. As previously pointed out, dipole moments are vector quantities. The ester link is no exception. X-ray diffraction studies show that, when the $\text{C}=\text{O}$ groups are spaced at an even number of chain atoms, dipole layers form which are tilted with respect to the fiber axis (Fig. 5-32a). Along with an identity period of

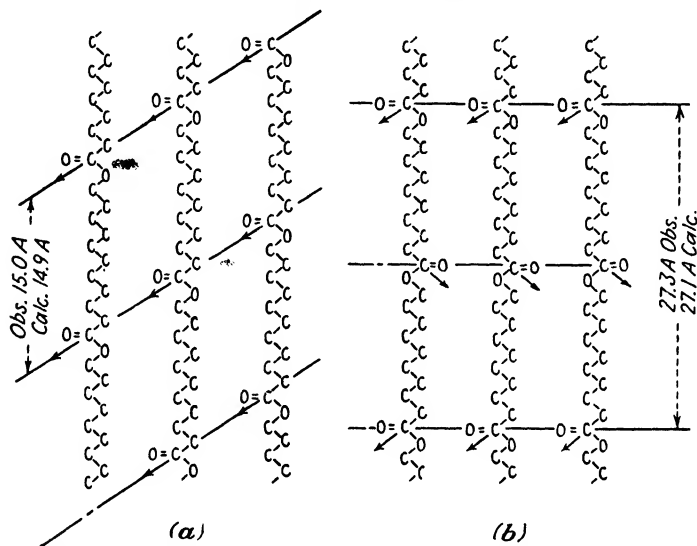


FIG. 5-32. Schematic formation of dipole layers. Arrows indicate dipole vectors. (a) Even number of chain atoms (polyundecanoate). (b) Odd number of chain atoms (polydecanoate). [C. S. Fuller and W. O. Baker, *J. Chem. Education*, **20**, 3 (1943).]

2.5 Å, a new fiber period appears in the x-ray photograph corresponding to the reflection arising from the atoms in the dipole layers. Since the $\text{C}=\text{O}$ groups occur always on the same side of the chains, one would expect that the fiber period would correspond to one mer. That this is indeed the case is confirmed by the fact that the measured and calculated values of this fiber period agree.

When the $\text{C}=\text{O}$ groups occur at an odd number of chain atoms, the dipole layers are perpendicular to the fiber axis and recurrence in space requires passing through two mers instead of one (Fig. 5-32b). Again there is excellent agreement between calculated and observed values. (See also the data on glycol-dibasic acid polyesters and synthetic polyamides in Table 5-3, page 169.)

This layering of polar groups in fibrous materials is a general phenomenon, and the type of layering is an important determinant of the physical properties of the material. Thus, in the tilted arrangement the dipoles act upon one another much more strongly and completely,

i.e., the intermolecular forces of attraction are greater, all other things being equal. This means higher melting point, lower solubility, greater stability and tensile strength, etc.

The synthetic polyamides (nylons) are strictly analogous to the polyesters just discussed except that amines are used in place of alcohols in their synthesis. Thus, bifunctional condensation of ω -aminocarboxylic

acids results in polyamides of the type $\text{—}\left[\text{HN}(\text{CH}_2)_x\overset{\text{O}}{\parallel}\text{C}\right]_n\text{—}$ whereas bi-bifunctional condensation of diamines and dicarboxylic acids produces

polymers with the formula $\text{—}\left[\text{HN}(\text{CH}_2)_x\text{NHC}(\text{CH}_2)_y\overset{\text{O}}{\parallel}\text{C}\right]_n\text{—}$. The only difference from the polyesters is the replacement of the chain oxygen by the NH group. This change is nevertheless highly important since extensive hydrogen bonding can take place between the C=O and NH groups on neighboring chains. As in the polyesters, tilted and perpendicular dipole layers may be observed in the diffraction patterns.

If a polyester or polyamide is melted and then rapidly quenched, the x-ray diffraction pattern of the fiber produced from the material is comparatively diffuse and imperfect. This is particularly noticeable in the polyamides, where the setting in of hydrogen bonding "freezes" sections of the chains in nonequilibrium positions. If the quenched fiber is then carefully annealed at elevated temperatures, the patterns rapidly grow sharper. The interpretation is that heating permits rotation of individual chain segments to take place, affording the polar groups the chance to associate. This results in more nearly perfect crystallization. But even very careful annealing does not bring about complete order.

The effect of stretching has already been discussed (Sec. 231). Stretching permits slippage to occur along the axis of drawing and results in more nearly perfect alignment of individual molecules and crystallites. Very high degrees of crystallinity are attainable (Fig. 5-29d).

The manifestation of quenched fiber patterns is a phenomenon encountered generally with all linear polymers. It is most noticeable when there are strong attractive centers, when the number of attractive centers is great, and when the symmetry of the chains is of high order. From the study of many x-ray diffraction patterns the conclusion to be drawn is that, even in the liquid state, segments of polymer molecules tend to arrange into definite, parallel bundles to form minute crystallites. Annealing simply permits greater order within each crystallite by allowing individual chain segments to rotate into their equilibrium lattice positions.

As previously stated, x-ray diffraction patterns indicate that, even

in the most highly crystallized and oriented fiber masses, amorphous regions are present (Fig. 2-9). Since molecular-weight determinations disclose the fact that the individual chains in the mass are much longer than the longest crystallite, one reaches the conclusion that the chains pass through several successive micellar and amorphous regions. Assume that one starts with a completely disordered melt and that, owing to cooling or drawing, crystallization begins. It will start at many points simultaneously. After a certain amount of crystallization has taken

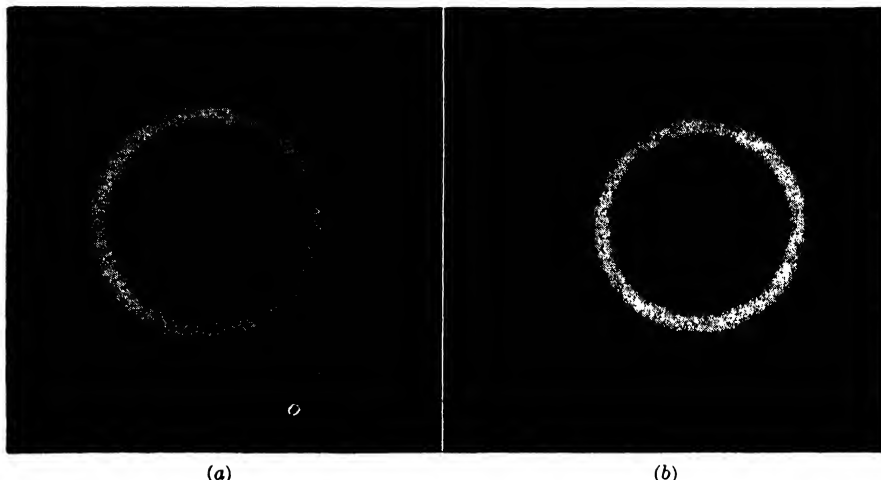


FIG. 5-33. X-ray diffraction patterns of synthetic space polymers. (a) Cast phenol-formaldehyde resin. (b) Cast polyester resin. (Courtesy of W. O. Baker and N. R. Pape, Bell Telephone Laboratories).

place, the chain molecules will, in a sense, be welded to one another at the crystallite regions and will become immobilized to such an extent that further chain alignment will become impossible—hence the existence of a “residue” of disordered, amorphous material. It is interesting to point out that the flexibility of fibers and the toughness and shock resistance of many plastics depend on just such a residue of amorphous, rubbery material between the crystallites. The amorphous regions act as minute shock absorbers.

523. Synthetic Space Polymers. When crystallization cannot be induced, relatively little precise information can be gleaned from x-ray photographs. Thus, synthetic resins of the thermosetting type are generally amorphous in advanced stages of polymerization (Fig. 5-33). Cross-linkage and polymer growth occur haphazardly (Secs. 408 *ff.*), the introduction of primary-valence restraints hinders molecular slippage, and the material is not orientable into crystalline, fibrous structures by externally applied stress (except for certain rubbers). Consequently,

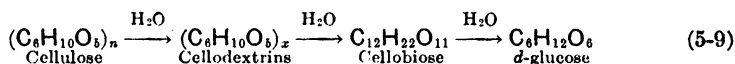
x-ray studies are not very helpful in establishing chemical and structural changes accompanying space polymerization. Furthermore, cross-linkage results in insolubility, tremendous disparity in molecular size and shape, and strong sorption of impurities and low-molecular-weight fractions. For all these reasons, precise elucidation of the physical and chemical nature of synthetic space polymers is very difficult.

Some natural space polymers are crystalline, *e.g.*, certain proteins and silicates. At the current writing, highly crystalline synthetic organic space polymers have not been produced.

STRUCTURES OF CELLULOSE AND CELLULOSIC FIBERS

Cellulose is used in tonnages greater by far than any other high polymer, and its structure has been the subject of intensive investigation.

524. Chemical Evidence. Cellulose is a carbohydrate with the empirical formula $(C_6H_{10}O_5)_n$. The $C_6H_{10}O_5$ unit has a molecular weight of 162 and is a trihydric alcohol, which may be written as $C_6H_7O_2(OH)_3$. Two of the alcohol groups are secondary, one primary. Cellulose may be hydrolytically degraded to various degrees.



The hydrolysis is acid catalyzed; and, with careful control, 95 per cent of the theoretical yield of glucose is obtainable.

From osmotic, ultracentrifuge, and solution-viscosity measurements the average molecular weight of native cellulose is variously found to be between 300,000 and 570,000, corresponding to a degree of polymerization of 1,800 to 3,500.

Before the advent of x-ray analyses, from a brilliant series of investigations chemists had concluded that cellulose is a long chain molecule with the structure 5-E on page 206. The linkage between the $C_6H_{10}O_5$ mers is a 1,4 linkage. The unit repeating in space along the chain is a cellobiose unit, $C_{12}H_{20}O_{10}$, consisting of two $C_6H_{10}O_5$ (anhydroglucose) mers. One of the two terminal mers of the chain is aldehydic [structure (5-E)]. Native cellulose exhibits an almost negligible ability to reduce Fehling's solution. The reducing power of its degradation products is greater since chain rupture results in more chain ends.

525. Evidence from Microscopy: Gross Structure. Cellulose fibers in a high state of purity may be obtained by removing a few per cent of impurities from raw cotton. A cotton fiber is a biologically organized structure. Light microscopy reveals that each single fiber is a tiny, long, hollow, flattened tube with a mild spiral twist. A central canal, or *lumen*, runs through the tube, and the tube has a kidney-shaped cross section

(Fig. 11-2). There is a thin *primary wall* with a closely joined *cuticle*, which incases the entire fiber. Between this primary wall and the lumen

is a thick layer called the *secondary wall*, which is the main constituent of the fiber.

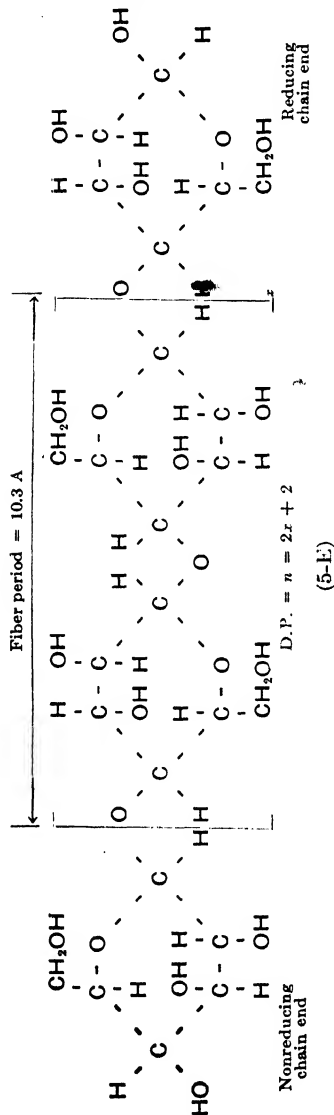
The primary wall of a cotton fiber is a membranous casing, the characteristics of which are different from those of the secondary wall. Although permeable, it swells much less in solvents and exerts a considerable mechanical restraint on the swelling of the fiber as a whole, directing it inward toward the lumen.

Photomicrographs reveal that the secondary wall contains a great number of interwoven subfibers called *fibrils*, which spiral along the main fiber axis (Fig. 11-11). The average angle between alternately spiraling fibrils is 57 deg (Fig. 5-34a). Furthermore, cellulose in the fibrils is doubly refractive (indicating orientation) and appears to be surrounded by smaller amounts of nondoubly refractive material. In other words, like all natural fibers, cotton is a highly organized, differentiated structure.

The fibrils in the cellulose fibers of linen and ramie do not spiral to nearly the same extent as in cotton. They lie more nearly parallel to the fiber axis (Table 9-6). Furthermore, the histological properties of linen and ramie differ from those of cotton.

The variations in the fibrillar and histological organization are important determinants of the considerable differences in mechanical properties and swelling characteristics exhibited by different natural cellulosic fibers (Appendix B).

Although it has been demonstrated that even artificial cellulosic fibers, the rayons, possess fibrillar organization, it is nevertheless true that their fibrillar organization is much less pronounced and that, in general, synthetic fibers are far more uniform masses than natural fibers.



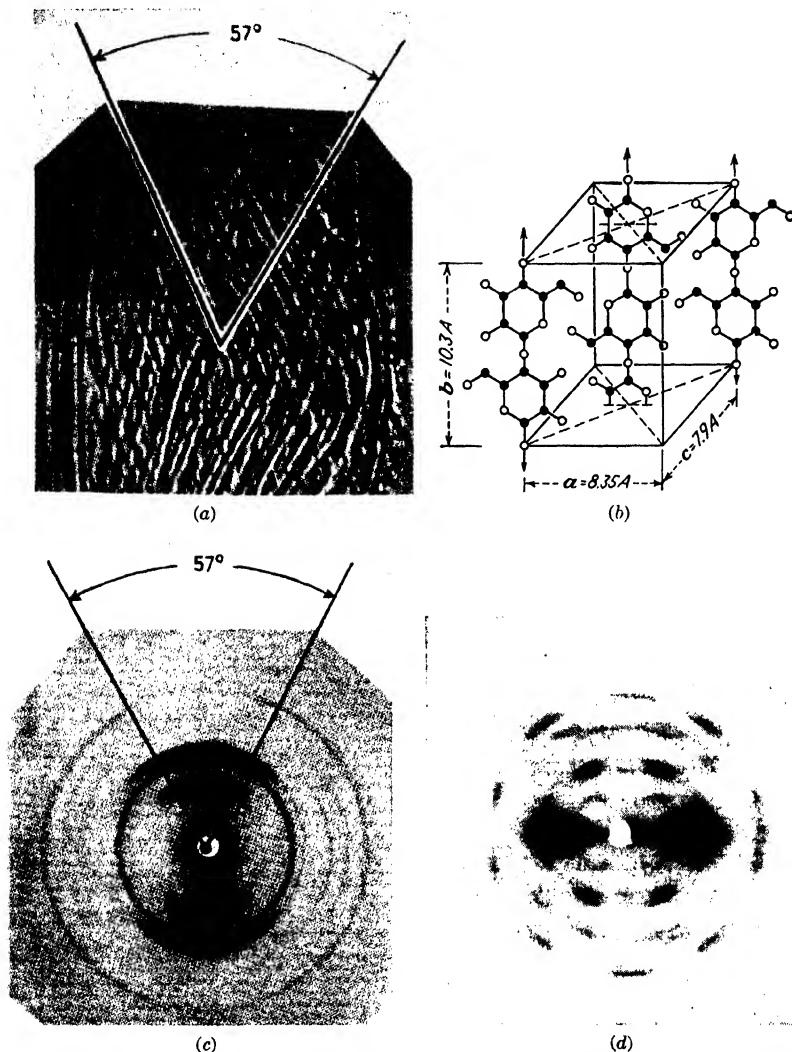


FIG. 5-34. Molecular and gross organization in cellulosic fibers. (a) Photomicrograph of a cotton fiber showing orientation of fibrils (fiber slightly swollen in phosphoric acid). (b) Unit cell of native cellulose. (c) X-ray fiber diagram of cotton. (d) X-ray fiber diagram of ramie. [(a) and (c) W. A. Sisson, *Contrib. Boyce Thompson Inst.*, **9**, 239 (1938). (b) K. K. Meyer and L. Misch, *Helv. Chim. Acta*, **20**, 232 (1937). (d) W. J. Lyons, *Sci. Monthly*, **54**, 238 (1942); photograph by E. E. Berkley.]

526. X-ray Diffraction Evidence. According to data on bond lengths and valence angles, the cellulose structure deduced from chemical evidence calls for a repetition of the cellobiose unit at a spacing of about 10.3 Å along the main fiber axis. This identity period is found in the x-ray

diagram (Table 5-3 and Fig. 5-34*b*). Indeed, the chemical evidence for the structure of cellulose is completely confirmed by x-ray analysis, which indicates that the cellulose molecule is long, mildly spiraled, and devoid of branching. A molecular model (Fig. 2-10, p. 56) shows that the anhydroglucose ($C_6H_{10}O_5$) units cannot rotate freely about the oxygen bridges because of steric hindrance.

Figure 5-34*c* is an x-ray fiber photograph of cotton fiber in its normal unstretched state. The background darkening shows the presence of some disordered amorphous material, while the well-defined arcs indicate that crystallites lie with a considerable degree of preferential alignment along the main fiber axis. (Random arrangement of the crystallites would result in complete concentric rings of uniform depth.) The angle subtended by the arcs in the x-ray diagram is the same as the average angle between cotton fibrils (Fig. 5-34*a*). From this it is concluded that in cotton the crystallites are aligned along the fibrils so that both the fibrils and the crystallites are arranged with the same spirality with respect to the main axis of the fiber. When a cotton fiber is subjected to a moderate tensile load, the arcs of the x-ray diagram temporarily foreshorten but return to their original value on release of the load. The accompanying elongation is due not so much to an internal intrinsic lengthening as to the spiraling fibrils (and crystallites) being temporarily pulled more nearly parallel to the main axis. In linen and ramie the cellulose crystallites also appear to be aligned along the fibrils; but since the latter do not spiral nearly so much with respect to the main fiber axis, the over-all degree of orientation is higher (Fig. 5-34*d*). Linen and ramie fibers are stronger in tension and less extensible than cotton fibers (Appendix B). They are also less pliable.

Viscose rayon and cuprammonium rayon fibers are made by precipitating cellulose from a liquid dispersion of a cellulosic derivative in which the chain molecules are in a high state of disorder. While the fibers of regenerated cellulose are still in a swollen condition they are subjected to elongation under tension. The degree of orientation in rayon fibers is consequently a variable depending upon the amount of drawing to which the material has been subjected (Fig. 5-35). There are crystallites and amorphous regions and fibrillar organization of a sort; but normally there is no central canal, nor is there any differentiation into primary and secondary walls, etc. Furthermore, the crystallites are a different allotropic modification from those of native cellulose (Sec. 527). As a consequence, the properties of rayon fibers are different from those of cotton and linen even though they all consist essentially of cellulose.

Molecular-weight determinations indicate that native cellulose molecules are of the order of 10,000 to 18,000 Å long. Quantitative evaluation of the x-ray diagrams of cotton fibers shows that the cellulose

crystallites are about 50 Å wide and only about 600 to 1,000 Å long. Furthermore, studies of the diffuse portions of the diagram indicate that in native cotton there is about 10 per cent of "amorphous" cellulose but that the chain molecules in this amorphous material are not entirely without order. The following analogy has been drawn. In the crystallites the molecular chains are regularly arranged like a handful of pencils of different lengths (no regular crystal faces). Here the structure is relatively dense and impenetrable. In the amorphous regions the chains lie in rough parallelism like a handful of twigs. The structure has order of a lower degree and is less dense, full of imperfections, and readily penetrated. This is experimental evidence in support of Fig. 2-9, where the (longer) chain molecules are pictured as passing successively through (shorter) crystallites and amorphous regions. Hydrolytic agents such as solutions of mineral acids rupture cellulose at the 1,4 oxygen linkages and depolymerize it to glucose. In terms of the above evidence one could reasonably expect that in a sample of cellulosic fiber this rupture and destruction would take place more rapidly in the amorphous regions. If this were the case, the fiber should break down to a powder of disconnected crystallites. This is indeed the case.

The deposition of minute heavy metal crystals within the cotton fiber

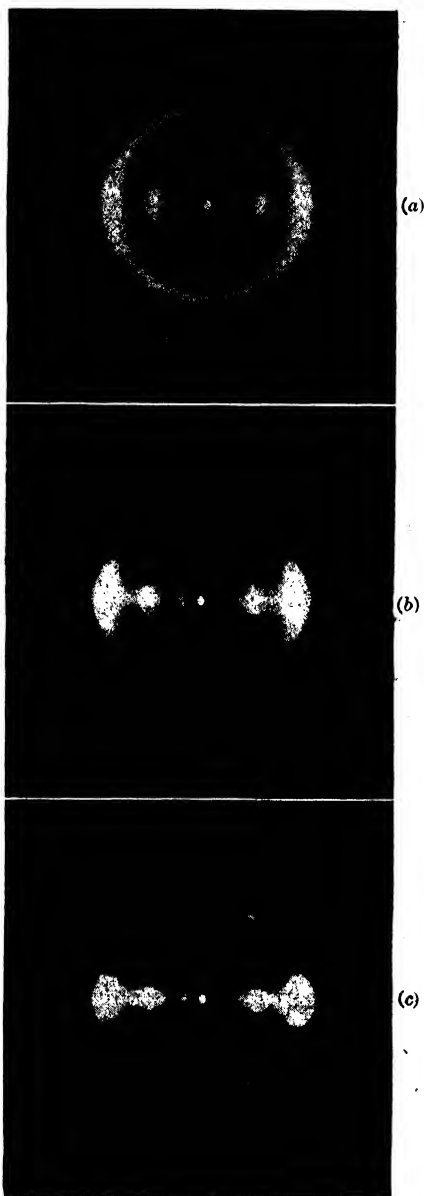


FIG. 5-35. Fiber patterns of regenerated cellulose (viscose rayon) fibers after various extents of stretching during manufacture. (a) Unstretched. (b) Moderately stretched. (c) Highly stretched. (Courtesy of American Viscose Corporation.)

(Sec. 509) discloses the presence of large lens-shaped holes about 200 Å in diameter and 1,000 Å long. Owing to these voids and the central canal a cellulose fiber is a somewhat expanded structure. This is true of

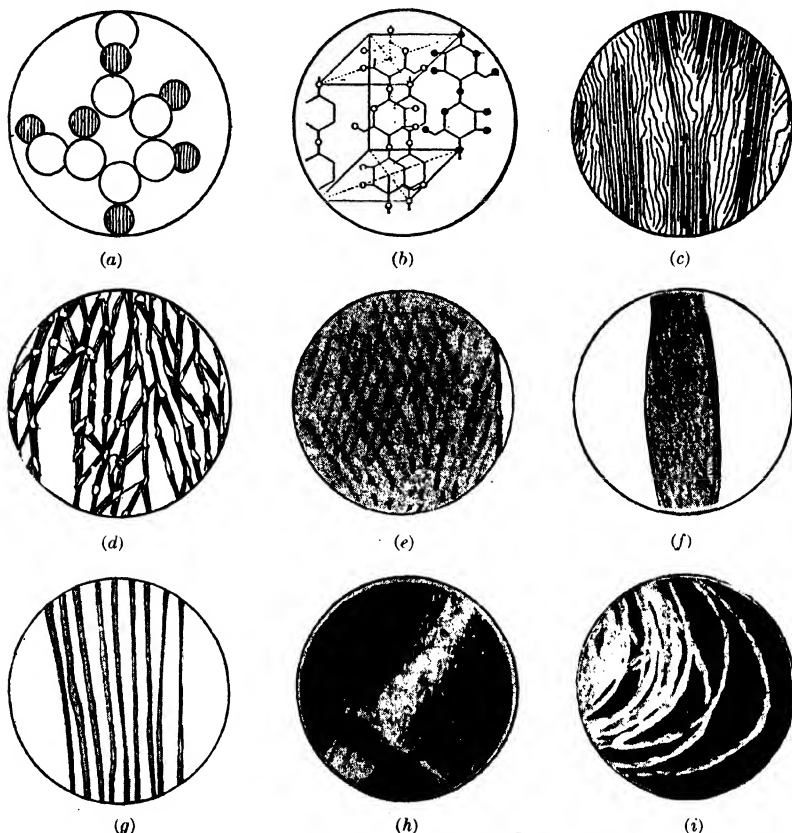


FIG. 5-36. Atomic, molecular, and gross organization in textile cellulose. Magnification decreases by a factor of 10 in passing from one illustration to the next. (a) Mer of the cellulose chain ($\times 10^8$); 1 Å = 1 cm. (b) Arrangement of the chains in the unit cell ($\times 10^7$); 10 Å = 1 cm. (c) Crystalline and amorphous regions in cellulose ($\times 10^6$); 100 Å = 1 cm. (d) Crystallites (series of parallel lines) and amorphous regions (irregular ovoids) comprising a network surrounding voids (lens shaped) ($\times 10^5$); 1,000 Å = 1 cm. (e) Fibrils that make up a single fiber ($\times 10^4$). This amplification represents the range of maximum resolution of the microscope; 10,000 Å = 1 cm. (f) Single fiber at microscope magnification ($\times 10^3$); 100,000 Å = 1 cm. (g) Group of fibers parallelized during textile manipulation ($\times 10^2$); 1,000,000 Å = 1 cm. (h) Yarn made by twisting together parallel fibers ($\times 10^1$); 10,000,000 Å = 1 cm. (i) Skein of viscose yarn as it appears to the naked eye ($\times 1$); 100,000,000 Å = 1 cm. [*H. Mark, J. Phys. Chem.*, **44**, 764 (1940).]

many other natural fibers. This expansion is an important determinant of mechanical behavior (Sec. 924).

Figure 5-36 summarizes current concepts of organization in cellulose starting with the atoms and ending with a skein of viscose rayon yarn.

The magnification decreases by a factor of 10 in passing from one illustration to the next.

527. Polymorphism in Cellulose. The crystallites of practically all naturally occurring celluloses exhibit the crystal form called the *native-cellulose* modification. The unit cell is rhombic and has the dimensions $a = 8.35$ Å, $b = 10.3$ Å (fiber period), $c = 7.9$ Å, as shown in Fig. 5-34*b*. If the cross section of a cellulose chain is represented by an oval, the arrangement in the unit cell of the native modification may be represented as shown in Fig. 5-37*a*. In native cellulose the angle $\beta = 89$ deg.

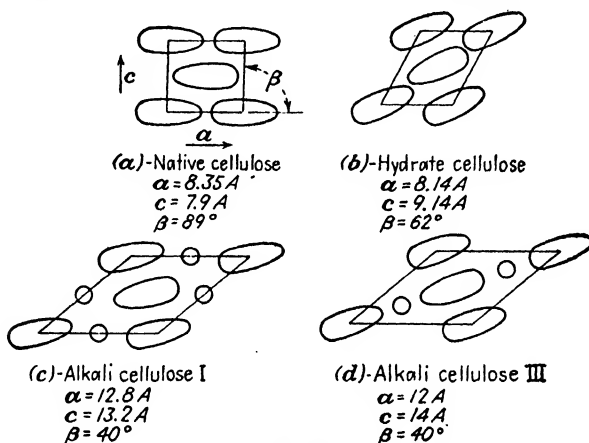


FIG. 5-37. Schematic projections of cellulose chains on the a - c plane perpendicular to the main fiber axis. Cellulose chains in cross section shown as ovals; ions or molecules of permutoid reactants shown as circles. (K. H. Meyer, "Natural and Synthetic Polymers," Interscience Publishers, Inc., New York, 1942.)

If cellulose is treated with a permutoid swelling or dispersing agent (Sec. 434) and then precipitated from solution or regenerated from an addition compound such as alkali cellulose, the chains associate into a new allotropic modification variously known as the *hydrate*-, *mercerized*-, or *regenerated-cellulose* modification. Analysis of the new x-ray pattern indicates that the space group is the same as that of native cellulose, the fiber period is still 10.3 Å; but the unit cell is monoclinic and has the dimensions $a = 8.14$ Å, $b = 10.3$ Å, $c = 9.14$ Å, and the angle β now equals 62 deg. Presumably the chains have rotated through an angle of 27 deg, and the arrangement is as shown in Fig. 5-37*b*.

Experiments indicate clearly that at high temperatures native cellulose is the stable form. It is more difficult to prove that this is also the case at room temperature, but the evidence currently at hand points in this direction. The structures of two typical permutoid swelling compounds, alkali cellulose I and alkali cellulose III, deduced from x-ray diffraction analysis are shown in Fig. 5-37. From these it will be readily

understood why the careful removal of the ions or molecules of the swelling agent (regeneration) predisposes the formation of hydrate cellulose even though it be the metastable modification. For example, if the caustic is removed from soda cellulose I by washing with cold water, only hydrate cellulose results. On the other hand, if it is decomposed with hot water, a mixture of native and hydrate cellulose forms.

Adsorption and reaction of nonpermutoid reagents with cellulose permit estimates to be made of the fraction of the total mers or hydroxyl groups that are free to react. If this fraction is taken as a measure of the internal surface, independent experiments indicate that the internal surface of regenerated cellulose is about double that of native cellulose; in the former, about half the total hydroxyl groups are exposed at surfaces, while in the latter only about one-fourth are free to react. Viscose rayon

fibers, cuprammonium rayon fibers, cellophane films, and mercerized cotton all exhibit the hydrate-cellulose form.

The two forms do not in any way differ as to the chemistry of the derivatives obtained from them, but hydrate cellulose is generally more reactive than native cellulose so that its behavior toward dyes, humidity, hydrolyzing agents, etc., is quite different, usually with respect to reaction rates.

STRUCTURES OF SILK AND WOOL

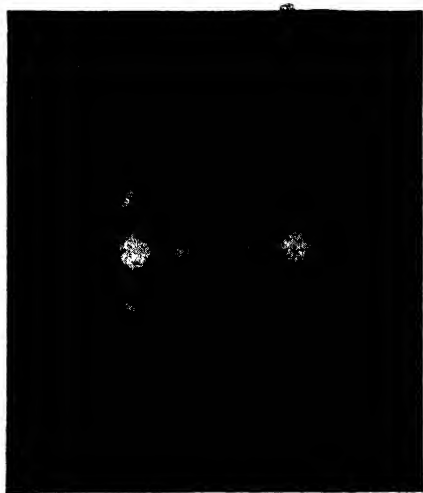


FIG. 5-38. X-ray fiber pattern of silk fibroin. (Courtesy of W. O. Baker and N. R. Pape, Bell Telephone Laboratories.)

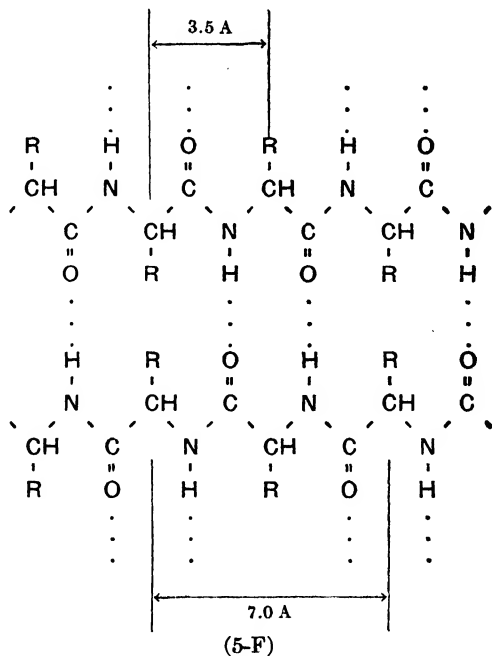
another protein, sericin (silk gum). The gum is easily removed by boiling the cocoons in soapy water, after which continuous single fibers, mostly 400 to 700 yd long, are obtained by a reeling process. These degummed silk fibroin fibers are the silk of commerce. They are smooth, fine, translucent, and devoid of spiral twist. The cross section is triangular to elliptical, there is no central canal, and the fibrillation is much less pronounced than that of cotton (Fig. 11-2). In this relative lack of morphological organization, they resemble the synthetic fibers. As protein fibers go, silk fibroin is uniquely simple as to chemical composition. It is built mainly from only four amino acids—glycine, alanine, serine, and tyrosine

528. Silk. The silkworm spins a double fiber in which two filaments composed of the protein silk fibroin are cemented together with

(Table 4-10). Glycine and alanine, the two simplest α -amino acids are present in a 2:1 ratio and account for over 75 mole per cent of the material.

Silk yields a fiber diagram from which it is clear that both amorphous and highly crystalline fractions are present (Fig. 5-38). Analysis of the x-ray pattern shows that the unit cell is small, and from its dimensions it seems that the crystallites are built up only of architecturally symmetrical glycyl and alanyl units, probably in a 1:1 ratio. The crystallites are at least 20 amino acid units long. Large structures such as tyrosine and arginine cannot be accommodated in the unit cell, and it follows that they must be concentrated in the amorphous regions. This is substantiated by various chemical behaviors; *e.g.*, hypobromite preferentially degrades the amorphous material, leaving crystallite leaflets that have the same x-ray spot pattern as silk and contain only glycyl and alanyl units.

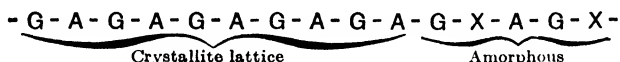
The fiber period of silk is 7.0 Å. This is precisely what it should be for fully extended linear glycyl-alanyl chains, as shown in structure (5-F).



The extensive hydrogen bridging between the chains accounts for the high tensile strength (Appendix B). The extended condition of the chains and the high degree of crystallite orientation account for the relatively low reversible extensibility (compared with wool).

The half fiber period, 3.5 Å, represents the length of one amino acid

residue and has been observed in other proteins. It is informative to represent the structure of the silk fibroin chain molecules schematically as follows:



where G is a glycine unit, A an alanine unit, X tyrosine, serine, etc., units.

In accordance with this schemat, in the crystallites there is a high degree of molecular symmetry and firm interchain hydrogen bridging, and the structure is dense and impenetrable. The glycyI and alanyl residues contain no free functional groups. By contrast, in the amorphous fractions, the symmetry is poor owing to the presence of tyrosyl and argininyI residues. The structure is comparatively open and contains the functional groups of the above residues as well as imperfectly bridged C=O and N—H groups on the main chains. Hence chemical reagents, dyes, swelling compounds, etc., are found to attack these regions preferentially.

529. Wool. As indicated in Table 4-10, wool is much more complex than silk. Chemical evidence for the complicated and ramiform structure of wool molecules has been presented in Secs. 445 ff.

At least three morphologically differentiated cellular layers are distinguishable in wool fibers by ordinary microscopy; an *epidermis* of flattened horny scales of nonbirefringent material (Fig. 11-2); a thick *cortex* of elongated, fibrillar cells, which are the main weight constituent; and an innermost marrow, or *medulla*, of cylindrical cells. The central medulla may be discontinuous or absent. In some wools the scales lie flat and tilelike; in others, they overlap, shinglelike, and protrude for part of their length, imparting a serrated character to the surface. This may cause wool fabric to scratch and irritate the skin. The horny epidermis exerts a restraining influence on the extension and retraction of the fiber. Its chemical composition differs from that of the cortex, and its permeability is different. The protruding scales of wool fibers are an important determinant of their excellent felting properties (Secs. 1130 ff.).

Astbury discovered that wool fibers in their normal unstretched condition yield an x-ray fiber diagram which he ascribed to a molecular arrangement which he called α -keratin (Fig. 5-39a). The pattern is not sharp, there is a great deal of background diffusion, and the photograph is difficult to analyze. This fits with the complex chemical composition [structure (4-M)]. There is a fiber period of 5.1 Å, quite different from that of silk fibroin (7.0 Å). Unlike silk, wool exhibits a high degree of reversible extensibility intermediate between that of normal fibers and rubbers. A moist wool fiber can be reversibly stretched to an elongation

of 80 per cent. If soaked in hot water, reversible extensions of 100 per cent are possible. In other words, the fiber exhibits a somewhat rubber-like elasticity and can be doubled in length without molecular slippage.

When wool fibers are held stretched to about double their normal length, the x-ray pattern changes greatly, indicating an extensive molecular rearrangement (Fig. 5-39b). Astbury called this the β -keratin structure. It has an identity spacing of 3.4 Å, close to the 3.5 Å of silk, and the pattern in other respects resembles that of silk. From this and chemical evidence it is clear that wool keratin like silk contains polypeptide chains in which the fundamental repeating structure is —NHCHRCO— .

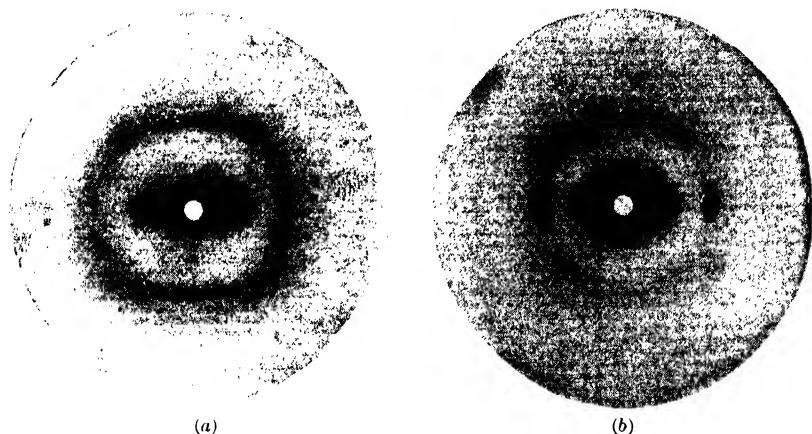


FIG. 5-39. X-ray fiber patterns of wool, (a) unstretched, and (b) stretched to 80% elongation. [W. T. Astbury and A. Street, *Trans. Roy. Soc. London*, **A230**, 75 (1931).]

In the β -keratin state the main chains are in their fully extended condition as in silk [structure (5-F)]. It also appears certain from steric considerations that the side chains (—R groups) are at right angles to the plane of the main chains and occur on alternate sides thereof, one "up," one "down."

In β -keratin, three successive amino acid residues represent a length of 10.2 Å (3×3.4 Å), which is just double the 5.1 Å fiber period of the α -keratin state. This suggests that α -keratin is a chain structure in which a three-peptide unit has become folded, spiralled or both, in such fashion that its length is half that of the extended state. The elongation of 100% is thus accounted for but at the current writing there is not sufficient evidence for precise elucidation of the nature of the α -keratin spiral or fold.

If a wool fiber is stretched and held in steam while the tension is released, it will *supercontract* to a length about one-third less even than its original α -keratin length. This supercontracted structure does not

reveal any new identity spacing; therefore, as with the α -keratin form itself, precise elucidation is not currently possible. Supercontraction of the steam-plasticized fiber may be due to a random folding of the chains. *Alternatively, it may have nothing whatever to do with molecular rearrangement and may be traceable merely to the release of the mechanical restraints normally exerted by the scaly epidermis when the wool fibers are not steam-plasticized.* This once again illustrates the potential importance of the morphological properties of a fiber.

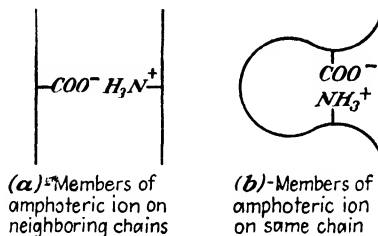


FIG. 5-40. Effects of salt bridging in proteins. (a) Interchain attraction. (b) Intrachain folding.

In true rubber, the spontaneous retraction from the stretched to the unstretched state on release of tension is attributable wholly to thermal agitation (Secs. 1219 *ff.*). The question is whether the same can be said for the spontaneous retraction of wool from the β - to the α -keratin state. The amphoteric ions of wool (Sec. 446) can promote both interchain attraction and intrachain folding or coiling, depending upon whether the carboxyl and amino groups are on neighboring chains or the same chain, as illustrated in Fig. 5-40.

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See also Appendix A, particularly Sec. A-5.

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CHAPTER 6

SOLUBILITY AND MOLECULAR-WEIGHT RELATIONS

600. In developing solubility equations for systems involving high polymers it has been found necessary to introduce new terms not required in describing the behavior of solutions of small molecules. These terms are needed because of the exaggerated effects produced upon the systems by the mere size of high polymers and the fact that their shape is a variable depending upon environment. In this chapter an attempt is made to present a concise statement of the extensions of classical theory required to obtain equations that satisfactorily cope with high-polymer solutions. Solubilities may be expressed in a variety of ways that may be divided into two general classes—volume and weight relationships. For various reasons one arrives at the mole fraction as the most desirable basis for developing equations for solutions, and most theoretical equations for low-molecular-weight systems express concentrations in this manner.

The mole fraction of a constituent is defined as follows:

$$N_s = \frac{n_s}{n}$$

where N_s is the mole fraction of component S , n_s the number of moles of component S , and n the total number of moles of all components.

It follows that

$$N_A + N_s + \cdots = 1 \quad (6-1a)$$

For a binary system containing only components A and S ,

$$N_A = 1 - N_s \quad (6-1b)$$

When one component is present in great excess and is termed the solvent, it is represented by subscript A . Unless otherwise stated, the word solution is used to mean a binary system.

In dealing with solutions of high polymers, it is frequently difficult to use mole fractions because of ignorance of the molecular weight of the material. Furthermore, in evaluating entropy effects the volume occupied by a molecule is more important than its weight. As a consequence, concentrations of high-polymer solutions are more advantageously expressed in terms of weight fractions and volume fractions.

The weight fraction of a component is

$$w_s = \frac{m_s}{m}$$

where w_s is the weight fraction of component S , m_s the mass of component S , and m the total mass of all components.

The volume fraction of a component is defined as follows:

$$V_s = \frac{V_s}{V}$$

where V_s is the volume fraction of component S , V_s the volume of component S , and V the total volume of all components.

SOLUTIONS OF LOW-MOLECULAR-WEIGHT SOLUTES

601. Perfect, or Ideal, Solutions. In the study of solutions, just as in the study of gases, it is best to consider first the ideal case and then to discuss deviations from it.

The simplest case of an ideal solution is represented by a mixture of two gases at low pressure. The molecules are relatively remote from each other so that the attractive forces, which fall off rapidly with distance, have no measurable effect and the fraction of the total volume occupied by the molecules themselves is negligible. Each behaves as if the others were absent, and both Dalton's additive pressure law and Amagat's additive volume law hold exactly.

Ideal liquid and solid mixtures behave in exactly the same way. The two components do not affect each other's behavior at all, except insofar as molecular concentrations are varied. However, it is difficult to picture such a simple state of affairs in real liquid or solid systems. Here the molecules are close to one another and affect the behavior of their neighbors to a measurable extent.

602. Types of Ideal Solutions. Since the proximity of the molecules of liquids and solids precludes the ideal case of no environmental effects such as exists in the perfect gas, the perfect liquid or solid solution must be defined as one in which a finite but constant environmental effect prevails throughout the entire range of composition. This constancy of environment may be realized in two ways, *viz.*:

1. By diluting the solute with such a large quantity of solvent that the solute molecule no longer exerts any measurable attractive or repulsive forces upon other solute molecules, and thus the constant environment of the solvent prevails. This is the basis of van't Hoff's theory of the infinitely dilute solution. *This type of solution is called the ideal dilute solution.*

2. By choosing components so similar in properties that a molecule

of either component will experience no change in the fields of force surrounding it when the composition is varied. *This is the perfect, or ideal, concentrated solution.* To meet these requirements there should be identical attractive forces between like and unlike molecules. Experimental criteria that may be used to identify a perfect solution are (1) complete miscibility, (2) no thermal change on mixing, (3) no volume change on mixing, and (4) similar molar volumes. (For spherical molecules it has been shown that a ratio of molecular volumes between 1 and 2 or a ratio of diameters between 1 and 1.26 is permissible.)

In view of the constant environment within all parts of such solutions, both types of molecules are randomly distributed, and the potential energy of a given molecule is not altered when one species among the surrounding molecules is replaced by another. Since most mixtures do not form ideal concentrated solutions, physical chemists have been limited in the main to dilute solutions to attain constant environmental conditions. In low-molecular-weight systems, solutions with solute concentrations of 1 mole per cent (about 1 per cent by weight or by volume) or less can usually be assumed to have the environment of the solvent.

603. State of Aggregation of Substances in Liquid Solution. Sometimes solids and gases dissolved in liquids form ideal solutions over their entire range of existence. In these cases there are thermal changes on mixing. Thus, when a solid is dissolved in a liquid, heat is generally absorbed; and if the solution behaves ideally, this heat of solution is identical with the heat of fusion of the solid. Also, when a gas is dissolved in a liquid, heat is evolved; and if the solution behaves ideally, this heat is identical with the heat of condensation of the gas. If the solid or gas is liquefied before addition to the solvent, the heat of mixing is zero. This demonstrates the important fact that the components of an ideal-liquid mixture exist in the liquid state in the solution, whatever their original states of aggregation.

604. The Mixture Rule. Ideal solutions obey the mixture rule, which, in its most general form, states that the properties of the mixture are the sum of the contributions of the separate components. Thus, for masses,

$$m = m_A + m_s = n_A M_A + n_s M_s \quad (6-2)$$

where M_A and M_s are the molecular weights of components A and S , respectively; for volumes,

$$V = V_A + V_s \quad (6-3)$$

and, for vapor pressures,

$$p = p_A + p_s = N_A p_A^0 + N_s p_s^0 \quad (6-4)$$

where p is the vapor pressure of the solution and p_A^0 and p_S^0 are the vapor pressures of pure components A and S , respectively. Equation (6-2) is obviously the law of the conservation of mass and applies to all solutions, perfect or otherwise. Equation (6-3) applies to "strictly regular" solutions (see below) as well as to perfect solutions. Equation (6-4) is the most important of the mixture rules. It is called the *general vapor-pressure law* or *Raoult's law* and *applies only to ideal concentrated solutions*.

605. Nonideal Solutions. Departure from ideal-solution behavior is a result of a lack of balance in the forces of attraction between like and unlike molecules in the system (Sec. 303). This may be manifested in heat effects, volume changes, viscosity effects, surface-tension abnormalities, or other departures from the mixture rule, but the most important manifestation from the standpoint of scientific study is departure from Raoult's law.

Two types of nonideal solutions are possible.

1. Solutions in which the like molecules attract each other more strongly than the unlike. In this case the like molecules tend to "squeeze out" the unlike. In the extreme, there is insolubility or immiscibility.

2. Solutions in which the unlike molecules attract one another more strongly than like molecules. In the extreme there is compound formation. (The solubility of salts in polar solvents is accounted for by the solvation of the ions, a process that provides sufficient energy for the dissociation of the crystal lattice.)

606. Regular Solutions. In either of the above types of nonideal solutions there is a tendency toward molecular aggregation and a non-random distribution of molecular types. If the unbalance in intermolecular forces of attraction is not too great, the tendency toward actual molecular aggregation may be overcome by thermal agitation. In such an instance it is possible to have a solution that does not obey Raoult's law but still meets some of the requirements for a perfect solution. This is a *regular solution*. Hildebrand first recognized the advantages of treating such solutions as a separate type. He defined a regular solution as one in which the entropy of mixing is the same as for an ideal solution of the same molar composition. This means that there is complete randomness of distribution of the different species of molecules present; *i.e.*, although there is a change of potential energy of a given molecule when one of its neighbors is changed, thermal agitation is able to prevent aggregation of like molecules. The heat of mixing is a measure of the deviation of a regular solution from ideal-solution behavior.

607. Vapor Pressures of Solutions. Consider the state of affairs at the surface of a pure liquid in equilibrium with its vapor. The rate of

evaporation obviously depends upon the number of molecules in the surface layer. If a solute is now added, some of the solvent molecules are displaced from the surface and the rate of evaporation of the solvent and its vapor pressure are reduced. This decrease in the vapor pressure of the solvent depends upon the amount of solute added, the size of the solute molecules, and the attractive forces between solvent and solute. If the solution is perfect, the concentration of solvent molecules in the surface is identical with their concentration in the interior and the solute

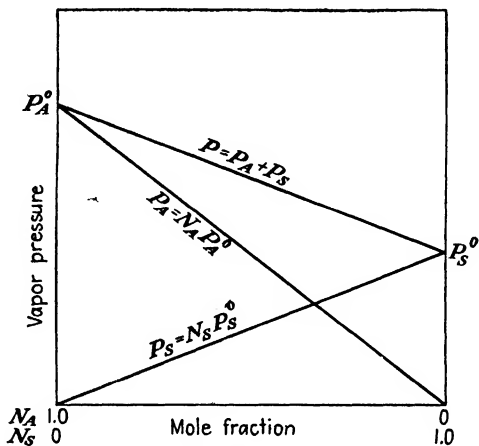


Fig. 6-1. Graphical representation of the general vapor-pressure law for a binary solution.

molecules exert neither a hindering nor an accelerating effect on the evaporation of the solvent molecules. If, furthermore, the vapor phase is an ideal gas, the rate of condensation (return to the solution) of the solvent molecules will be neither hindered nor accelerated by any molecules that may be present in the vapor phase.

When all the above conditions are met, Raoult's law holds; *i.e.*,

$$p_A = N_A p_A^0 \quad p_S = N_S p_S^0 \quad (6-5)$$

and

$$p = p_A + p_S = N_A p_A^0 + N_S p_S^0$$

Figure 6-1 is a graph of this relationship. This law has been experimentally confirmed for a number of binary systems such as benzene-toluene and chlorobenzene-bromobenzene. The components of such systems resemble each other closely in chemical structure, composition, and molecular size, and the solution might reasonably be expected to behave ideally.

If a nonvolatile solute is used, the vapor is composed entirely of solvent molecules and p equals p_A . Therefore, in this case

$$p = N_A p_A^0 = (1 - N_S) p_A^0 \quad (6-6a)$$

from which

$$N_s = 1 - \frac{p}{p_A^0} = \frac{\Delta p}{p_A^0}$$

or

$$\Delta p = N_s p_A^0 \quad (6-6b)$$

Equation (6-6b) states that the lowering of the vapor pressure by a non-volatile solute is proportional to the mole fraction of the solute if the solution is perfect and the vapor obeys the perfect-gas law. The latter usually offers no difficulty because, for practically all solutions below the normal boiling point, the vapor concentrations are so low that the perfect-gas law is obeyed. However, to attain perfect-solution behavior, most solutions must be made dilute. For dilute solutions, that is, 0.01 mole fraction or less of solute,

$$N_s = \frac{n_s}{n_A + n_s} \cong \frac{n_s}{n_A}$$

and Eq. (6-6b) reduces to

$$\frac{n_s}{n_A} = \frac{\Delta p}{p_A^0} \quad (6-7)$$

Equation (6-7) is the initial form in which Raoult stated his law. It is obvious that this relationship affords a method of determining molecular weight.

Since very few solutions are ideal over the entire range of concentrations, deviations from Raoult's law are common. Figure 6-2 is a graph of a system that illustrates one type of deviation. The dotted lines show what the vapor pressures of the components would be if they obeyed Raoult's law. This is a common type of system in which both components exhibit negative deviations, the result of greater attraction between unlike than between like molecules.

Examination of Fig. 6-2 in the dilute-solution regions shows that the curves for the solvent (substance present in high concentration) approach the theoretical line of Raoult's law. In other words, as stated earlier, the solvent behaves perfectly in all very dilute solutions. It will also be noted that in the dilute-solution regions the curve for the solute (substance present in low concentration) approaches a straight line *but not the line of Raoult's law*. This straight-line behavior (Henry's law) is to be expected since this is a region of essentially constant environment. However, it is not the straight line of Raoult's law since this would be found in the environment of the pure solute, whereas the environment is actually that of the pure solvent.

608. Partial Properties. In dealing with any but perfect solutions one cannot use as the molal value of any property of a component the

value of that property in the pure state. The presence of the other components of the solution changes the environment and affects the magnitude of the property. In other words, the mixture rule does not hold. For example, in the pure state, the molal volume of component S is $V_{M,S} = V_s/n_s$. In solution, the corresponding property is called the

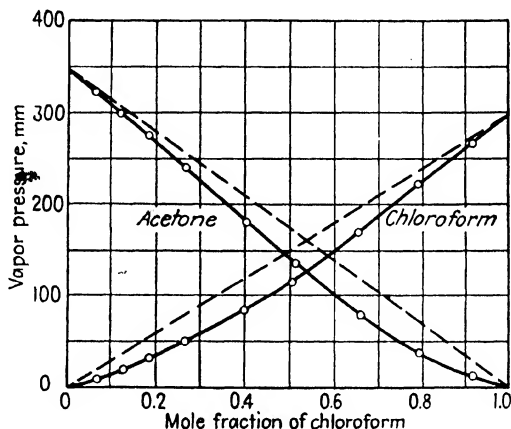


FIG. 6-2. Partial vapor pressures of one type of nonideal liquid mixture. (*J. H. Hildebrand, "Solubility of Nonelectrolytes," Reinhold Publishing Corporation, 1936.*)

partial molal volume of S , designated by the symbol $\bar{V}_{M,S}$, and is defined analytically as follows:

$$\bar{V}_{M,S} = \left(\frac{\partial V}{\partial n_S} \right)_{T,p,n_A} \quad (6-8)$$

If a small number of moles of component S are added to a large amount of solution so that the environment remains essentially unaltered, the increase in volume is $n_S \bar{V}_{M,S}$. Addition of component A would cause an increase in volume $n_A \bar{V}_{M,A}$. This concept of partial molal quantities is valuable in that it enables us to use equations of the simple, convenient mixture-rule form. Thus, from the above, it follows that in any solution

$$V = n_A \bar{V}_{M,A} + n_S \bar{V}_{M,S} \quad (6-9)$$

Other partial molal extensive properties such as partial molal heat capacities, and the like, are similarly defined. For example, partial molal enthalpies of solution components are

$$\bar{H}_A = \left(\frac{\partial H}{\partial n_A} \right)_{n_S} \quad \bar{H}_S = \left(\frac{\partial H}{\partial n_S} \right)_{n_A}$$

and the total enthalpy of the solution is

$$H = n_A \bar{H}_A + n_S \bar{H}_S \quad (6-10)$$

However, because enthalpy is of unknown absolute magnitude Eq. (6-10) is not of practical use until a convenient appropriate standard state is adopted for each component. A more useful equation is the enthalpy of formation of a solution from its components.

$$H = n_A(\bar{H}_A - H_A) + n_S(\bar{H}_S - H_S) = n_A\Delta\bar{H}_A + n_S\Delta\bar{H}_S \quad (6-11)$$

where H_A and H_S are the molal enthalpies of the components in their standard states, and $\Delta\bar{H}_A$ and $\Delta\bar{H}_S$ are the partial molal heats of mixing of the components.

609. Activity. Because solutions are not ideal, except in rare cases, equations like Eq. (6-5) are not applicable at high concentrations or even for exact calculations at low concentrations. More complicated equations, either based on theory or entirely empirical, must be used. In gaseous systems, the well-known van der Waals equation is a typical example. To preserve *apparent* simplicity in equations that account for departure from perfect-solution behavior, a correction term known as the *activity* is introduced in place of concentration. Thus, in the general vapor-pressure law,

$$p_A = a_A p_A^0 \quad p_S = a_S p_S^0 \quad (6-12a)$$

and

$$p = a_A p_A^0 + a_S p_S^0 \quad (6-12b)$$

where a_A and a_S are the activities of solvent and solute, respectively. They are experimentally determined functions which correct for the deviations from perfect behavior in such fashion that the actual behavior of the system is expressed by a mathematical equation which preserves the outward form of the equation describing the behavior of a perfect system. (These statements should be regarded, not as the formal definition of activity, but as deductions from the thermodynamic definition. Strictly speaking, activity is defined in terms of the free-energy change during dilution of a solution.)

For regular solutions,

$$\ln a_A = \ln N_A + \frac{\Delta\bar{H}_A}{RT} \quad (6-13)$$

where \bar{H}_A is the partial molal heat of mixing of component A in the solution. This equation will not hold for concentrated solutions, especially if the heat of mixing is negative.

Activities are calculated from the actual deviations of the system from perfect behavior. The ratio of activity to mole fraction is called the *activity coefficient*.

$$\gamma = \frac{a}{N}$$

From this it follows that

$$\gamma_A = \frac{p_A}{p_A^0 N_A} \quad \gamma_S = \frac{p_S}{p_S^0 N_S} \quad (6-14)$$

Figure 6-3 is a graph of activities vs. concentrations in mercury-tin amalgams as calculated by means of Eq. (6-14). The dashed lines represent ideal behavior for which $a = N$ and $\gamma = 1$.

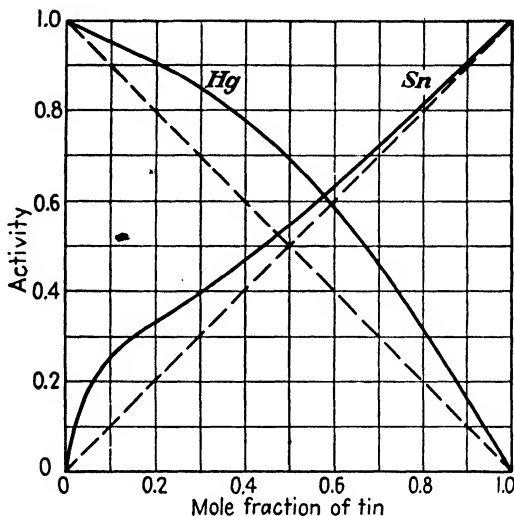


FIG. 6-3. Activities in mercury-tin amalgam at 323 C. (*J. H. Hildebrand, "Solubility of Nonelectrolytes," Reinhold Publishing Corporation, New York, 1936.*)

Activities are extremely useful for calculation purposes, as will be evident in subsequent sections.

SOLUTIONS OF HIGH-POLYMER SOLUTES

It will be helpful to point out the factors that distinguish polymer solutions from solutions of low-molecular-weight solutes (see also Secs. 300 to 316).

610. Effect of Molecular Volume. The entire theory of ideal solutions of low-molecular-weight substances is based on the substitution of a solvent molecule by a solute molecule without change in environment. Naturally, this replacement requires similar molar volumes, a condition that cannot occur in solutions of high polymers. This in itself causes deviations from ideal behavior even at extremely low concentrations.

A 1 mole per cent solution, which normally would exhibit perfect-solution behavior in the case of a low-molecular-weight solute, often represents an impossible concentration for a high-polymer solute. Thus, if the molecular weight of the solute were 100,000 and that of the solvent

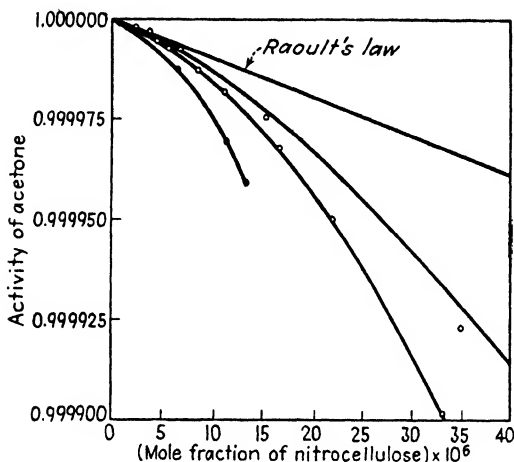


FIG. 6-4. Activities of acetone in solutions of three samples of cellulose nitrate. [M. L. Huggins, *J. Am. Chem. Soc.*, **64**, 1712 (1942).]

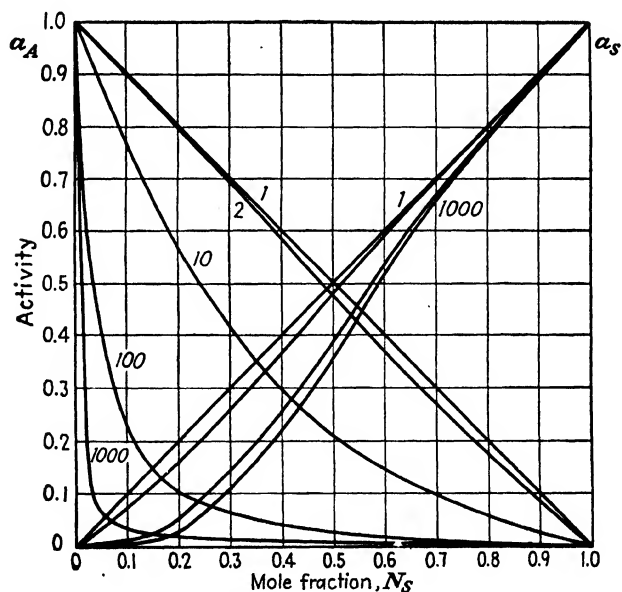


FIG. 6-5. Theoretical curves of activity as a function of mole fraction with certain values of the partial molal volume ratio, \bar{V}_s/\bar{V}_A . [M. L. Huggins, *Ann. N. Y. Acad. Sci.*, **44**, 431 (1943).]

100, a solution of the above concentration would contain ten times as much solute as solvent. Consequently, in high-polymer solutions the weight fraction (or volume fraction) is a much better measure of the relative environmental effects of the components. A 1 wt. per cent solution of the above system would have a mole fraction of solute of approximately 0.00001. That even this low concentration is not sufficiently dilute for high polymers is indicated by Fig. 6-4. Indeed, only an infinitely dilute high-polymer solution is sufficiently dilute for application of the ordinary thermodynamic equations applicable to small molecules.

A theoretical consideration of the effect of the volume of a chain-type solute in an otherwise ideal system leads to the following equation:

$$\ln a_A = \ln V_A + \left(1 - \frac{\bar{V}_A}{\bar{V}_s}\right) V_s \quad (6-15)$$

where \bar{V}_A and \bar{V}_s are partial molal volumes and V_A and V_s are volume fractions. An analogous equation applies for the activity of the solute. The effect of volume ratio on the activity is given by Fig. 6-5.

611. Effect of Intermolecular Forces. Like low-molecular-weight solutions (Sec. 605), high-polymer solutions exhibit deviations when there is a lack of balance in the forces of attraction between like and unlike molecules in the system. If the solution is otherwise regular, the following equation has been shown to hold:

$$\ln a_A = \ln V_A + \left(1 - \frac{\bar{V}_A}{\bar{V}_s}\right) V_s + \mu_A V_s^2 \quad (6-16)$$

where μ_A is a constant, characteristic of the pair of components and the temperature. An analogous equation applies for the activity of the solute. The effect of μ_A on the activity, the volume ratio remaining constant, is given by Fig. 6-6.

Equation (6-16) has been found to agree with experiment for a wide variety of systems. Thus in Fig. 6-4 the three lower curves are not drawn through the experimental points but represent graphs of Eq. (6-16) for selected values of μ_A .

FREEZING POINT AND SOLUBILITY

612. Freezing-point Depression. The melting point of a pure substance is a constant characteristic of the material. It is frequently used as an index of purity since impurities generally lower the melting point. One exception is an impurity that does not dissolve in the molten substance. This has no effect on the melting point. Another exception is an impurity that enters the crystal phase of the original material, *i.e.*,

forms a solid solution. This may raise or lower the melting point or have no effect whatever.

Consider a solution of two components *A* and *S*. Pure *A* has its characteristic melting point, which is depressed on addition of *S*. Similarly, pure *S* has its characteristic melting point, which is depressed on addition of *A*. The freezing-point diagram of this system (Fig. 6-7)

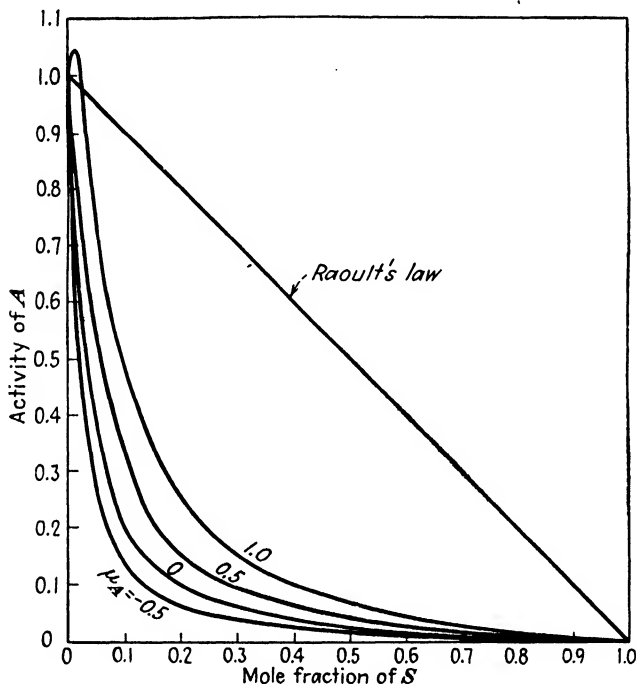


FIG. 6-6. Theoretical curves of activity of solvent as a function of mole fraction for \bar{V}_S/\bar{V}_A constant and equal to 100, with certain values of μ_A . [M. L. Huggins, *Ann. N. Y. Acad. Sci.*, **44**, 431 (1943).]

therefore consists of two curves, one of which (curve *A*) represents the temperatures at which solutions of varying composition are in equilibrium with crystals of component *A* and the other (curve *S*) temperatures at which solutions are in equilibrium with crystals of component *S*. The two curves intersect at the so-called "eutectic point," which is the lowest melting point possible. At the eutectic point the solution is in equilibrium with crystals of both components, and the solution has the same composition as the mixture of solid crystals with which it is in equilibrium. Freezing-point diagrams of polyethylene glycol-water systems are given in Fig. 6-8.

Thermodynamically, the freezing-point depression is related to the

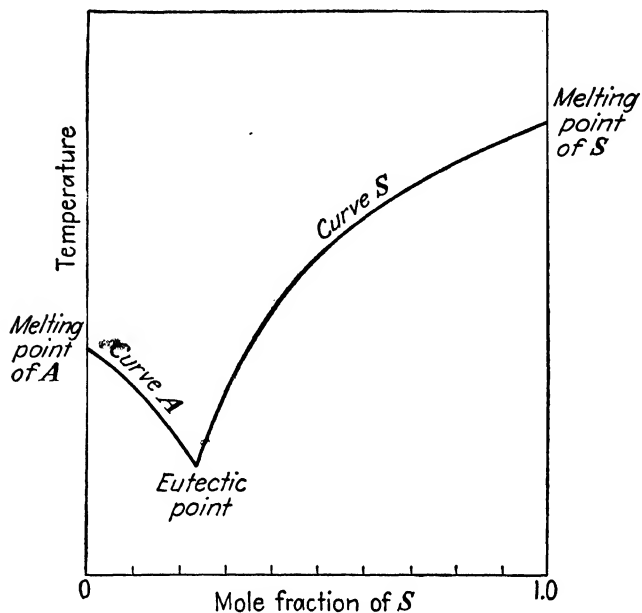
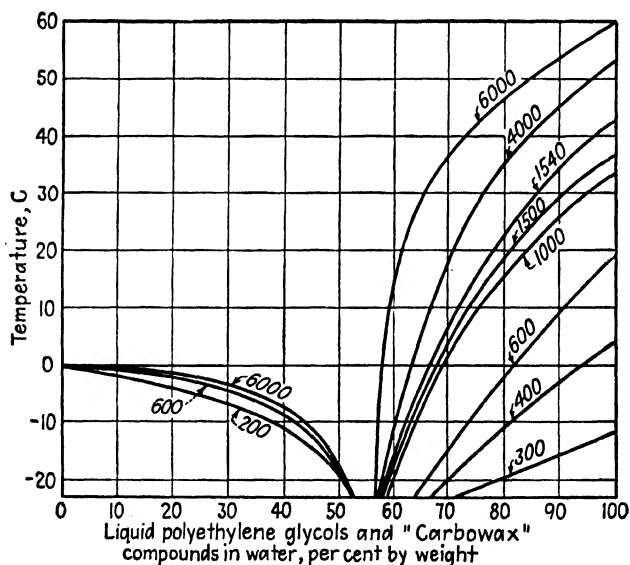


FIG. 6-7. General freezing-point diagram for a binary solution.

FIG. 6-8. Freezing-point diagrams of a homologous series of polymers and water. Numbers on curves are average molecular weights. Below -23°C all mixtures supercool and have no definite freezing point. (Courtesy of Carbide and Carbon Chemicals Corp.)

vapor-pressure lowering, and the laws governing the one property are derivable from those of the other. For example, it can be shown that the equation for the freezing-point curve of A (Fig. 6-7) is

$$\frac{1}{T} - \frac{1}{T_f} = - \frac{R}{\Delta H_{f,A}} \ln N_A \quad (6-17)$$

where T is the freezing point of the solution, T_f the freezing point of pure A , $\Delta H_{f,A}$ the molar heat of fusion of A (*i.e.*, the heat of solution), R the molar gas constant, and N_A the mole fraction of A in the solution.

Since $T_f - T$ is Δt_f , the freezing-point depression, it will be seen that Eq. (6-17) correlates this depression with the composition of the solution and thus affords a means of determining molecular weights. This equation holds only for perfect solutions (in the absence of solid-solution formation)—a very drastic limitation. For nonideal solutions,

$$\frac{1}{T} - \frac{1}{T_f} = - \frac{R}{\Delta \bar{H}_{f,A}} \ln a_A \quad (6-18)$$

where $\Delta \bar{H}_{f,A}$ is the partial molal heat of solution and a_A is the activity of component A .

The usefulness of the activity function is evident from this equation. The activity may be determined by an independent method, *e.g.*, by vapor-pressure depression, and used in Eq. (6-18). This enables the calculation of the freezing-point depression no matter what the character of the solution, whether nonperfect solutions of small molecules, solutions containing high polymers, etc.

In very dilute solutions, the freezing-point equation reduces to the form

$$\Delta t_f = K_{f,A} C = \frac{K_{f,A}}{M_s} c \quad (6-19)$$

where $K_{f,A}$ is the freezing-point depression constant, a constant characteristic of the solvent, *i.e.*, the substance freezing out, C the molar concentration of the solute, *i.e.*, moles of solute per unit volume of solution, and c the weight concentration of the solute, *i.e.*, mass of solute per unit volume of solution.

613. Solubility Relationships. Freezing-point depression curves such as are given in Figs. 6-7 and 6-8 are also solubility curves. Thus, in Fig. 6-7, curve S represents the depression of the freezing point of S as A is added. But, since the solid in equilibrium with the solution is substance S , the solution must evidently be saturated with this material so that curve S may just as logically be labeled "solubility curve of S ." Consequently, the freezing-point depression equation is also the solubility

equation. If emphasis is placed upon solubility, the equation is more commonly written

$$\ln N_{s,\text{sat}} = -\frac{\Delta H_{f,s}}{R} \left(\frac{1}{T} - \frac{1}{T_f} \right) \quad (6-20)$$

Since perfect solutions are relatively rare, this equation again has only limited applicability. Nevertheless, by the use of empirical constants such an equation may be made to represent fairly accurately the solubility relations of a great many mixtures, provided that dissociation or compound formation does not occur. Thus,

$$\ln N_s = \frac{A}{RT} + C \quad (6-21)$$

where A and C are empirical constants.

Figure 6-9 illustrates the applicability of this equation to hydrocarbon solids. Paraffin waxes, pure paraffin hydrocarbons, and polyethylene resins all follow this relationship exactly. It will be noticed that all the solubility curves for the polyethylenes meet, on extrapolation, at a common point, which from Eq. (6-20) should be the melting point. The melting-point temperature given by the solubility curves is 112 C, which is in excellent agreement with other values (Table 5-8, page 182).

It has been previously pointed out that in a homologous series of organic compounds the heats of fusion increase with molecular weight in accordance with the following empirical equation (see Eq. 2-3, p. 43):

$$H_f = q'M \quad (6-22)$$

where M is the molecular weight and q' is an experimental constant for the particular homologous series. Substituting into Eq. (6-20) yields an equation relating solubility, temperature, and molecular weight.

$$\ln N_s = -\frac{q'M}{R} \left(\frac{1}{T} - \frac{1}{T_f} \right) \quad (6-23)$$

Evaluation of the slopes of the solubility lines of Fig. 6-9 indicates that this equation is applicable, the values of q' being essentially constant for each of the three hydrocarbon types. Since, for dilute solutions, mole fraction is proportional to weight fraction, $\log w_s$ vs. $1/T$ is also a straight line for polymer solutions.

High polymers are frequently dissolved in a mixture of solvents, particularly a mixture of a good solvent A and a "nonsolvent" B . The heat of solution of many pure crystalline high polymers in such a solvent mixture has been shown to obey the equation

$$H_f = (q' + p'V_B)M \quad (6-24)$$

where V_B is the volume fraction of nonsolvent B and q' and p' are experimental constants.

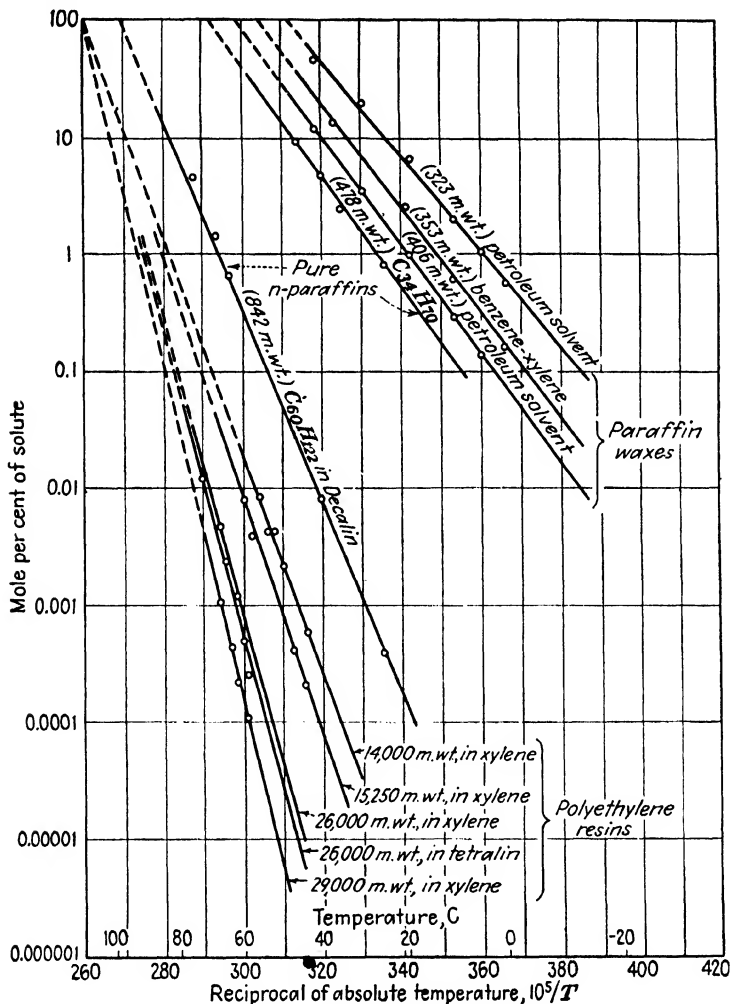


FIG. 6-9. Solubility of n -paraffins in aromatic hydrocarbons. [A. E. Matbauer and C. S. Myers, *Trans. Electrochem. Soc.*, **90**, 341 (1946).]

Substituting Eq. (6-24) into (6-20) and combining empirical constants, one obtains for a pure high polymer at constant temperature

$$\ln N_s = D + EV_B^* \quad (6-25)$$

where V_B^* is the *precipitability*, which is the volume fraction of nonsolvent in the mixture at the first detectable precipitation. This equation pre-

dicts that the plot of $\log N_{\text{sat}}$ (or $\log w_{\text{sat}}$) vs. V_B is a straight line. This relationship is established by Fig. 6-10, giving the solubility of several polyethylene glycols in a mixture of methanol (solvent) and ether (nonsolvent).

Figure 6-10 also brings out a remarkable property of such high-polymer solutions. It will be noticed that the solubility lines are almost horizontal. This means that, for a particular high polymer, mixtures of *A* and *B* containing more than a critical concentration of *A* will be good solvents, while mixtures containing less than this concentration will be poor solvents. On starting with a given constant initial concentration of a high polymer in solvent *A* and adding *B*, the following relationship applies:

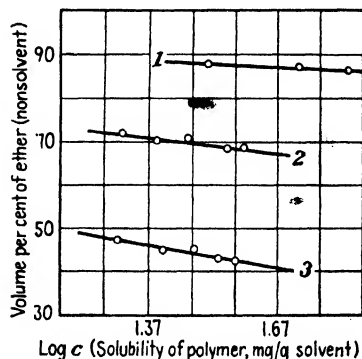


FIG. 6-10. Solubility of polyethylene glycols in methanol-ether mixtures. Curve 1: D.P. = 18. Curve 2: D.P. = 42. Curve 3: D.P. = 90. [E. L. Lovell and H. Hibbert, *J. Am. Chem. Soc.*, **61**, 1916 (1939).]

$$V_B^* = \alpha + \frac{\beta}{M} \quad (6-26)$$

where α and β are empirical constants for a given homologous series. Figure 6-11 shows regions of validity of this equation for a highly crystalline (but not fractionated) material, polyundecanoate.

614. Fractionation of High Polymers. Synthetic high polymers and degraded natural high polymers contain molecules covering a range of molecular weights. The most commonly used method of fractionating such a mixture into cuts with narrow ranges of molecular weights takes advantage of the effect described in the preceding section. The material is dissolved in a good solvent *A*, and successive amounts of a nonsolvent *B* are added. On adding the first small amount of *B*, only material of relatively high molecular weight precipitates. This is separated and a further amount of *B* added, which throws out a second fraction with a somewhat lower degree of polymerization. (Purer products are obtained if, after adding the nonsolvent, the mix-

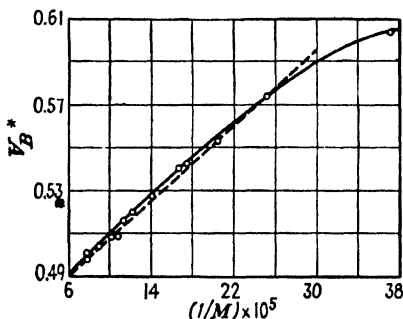


FIG. 6-11. Precipitability of polyundecanoates as a function of molecular weight. [W. O. Baker, C. S. Fuller, and J. H. Heiss, Jr., *J. Am. Chem. Soc.*, **63**, 2142 (1941).]

ture is warmed to a temperature at which it becomes homogeneous and the polymer is then allowed to precipitate as the mixture cools.) These fractions are more homogeneous than the original material but are still not entirely "pure." By repetition of the procedure, products may be obtained with very narrow molecular-weight ranges. This technique is used both to determine molecular-weight distribution curves and to prepare homogeneous polymer samples for special studies.

It must be recognized that this technique separates the various species of molecules according to their solubility characteristics rather than their molecular weight alone. Branching, catalyst fragments, chemical reactions during degradation, etc., will confer different solubility characteristics upon polymer molecules. For these reasons, different fractionation procedures may produce different molecular-weight distribution curves, and samples prepared by fractionation are not necessarily completely homogeneous.

High polymers may also be fractionated by differential solution. This technique is commonly used to divide a material into soluble and insoluble portions; *e.g.*, a *sol fraction* is made by extracting raw rubber with ethyl ether or petroleum ether, the insoluble residue being the *gel fraction*.

MOLECULAR WEIGHTS OF HIGH POLYMERS

615. Many chemical advances have been won through studies of the molecular weights of small molecules. Such studies have served both to elucidate molecular structure and composition and to test physicochemical hypotheses. Molecular-weight studies do not assume equal importance in the field of high polymers, although one would not by any means dismiss them as being without value. For one thing, many of the significant properties vary but slightly with molecular weight once a certain minimum degree of polymerization has been attained. Moreover, high polymers contain molecules of different sizes so that the measured molecular weight is at best a mean value; and, for the exact characterization of the material, the size distribution of the molecules must also be known.

For many industrial preparations it is sufficient to know only the order of the molecular weight, and it is frequently more convenient to measure properties that *depend* upon the molecular weight rather than the molecular weight itself. The property most often exploited for this purpose is the intrinsic viscosity [Eq. (6-44), page 248].

616. General Classification of Molecular-weight Methods. One way of deducing molecular weights of high polymers is to determine the number of terminal groups. These so-called *end-group methods* depend

on the existence of terminal functional groups that remain after polymerization or are formed by blocking agents, the important point being that the end mers are left detectably different from the intermediate mers. A list of applications is presented in Table 6-1. Carothers' work

TABLE 6-1. END-GROUP METHODS OF MOLECULAR-WEIGHT DETERMINATION

Polymer	Reacting end group	Methods
Hydroxy acid polyesters and amino acid polyamides	—COOH	a. Acid determination b. Salt formation and subsequent determination of metal content
Amino acid polyamides.....	—NH ₂	Primary amino group determination
Glycol polyethers.....	—OH	Acid take-up during acetylation
Cellulose.....	Reducing end [structure (5-E)]	a. Copper number b. Oxidation to carboxyl and subsequent acid determination c. Reaction with mercaptan and subsequent sulfur determination
Cellulose.....	4 OH's on one end. 3 OH's on other mers	Methylation, hydrolysis, and isolation of tetramethyl glucose
End-blocked polymers: Diamine-dicarboxylic acid polyamides blocked with acetic acid	—OOCCH ₃	Acetate determination
Dimethylsiloxanes, ethoxy end blocked	—OC ₂ H ₅	Ethoxy determination
Ethylene.....	—CH ₃	Infrared spectrum

on acidic polyethylene succinates summarized in Table 1-3, p. 13, is an example. Such methods are not always successful or applicable for the following reasons: (1) end groups are not always detectable, (2) purification of the mass is often impossible, and (3) branching may result in more than two "ends." End-group determinations are often, but not always, chemical, and as a class they are differentiated from the more usual procedures that may be referred to as physical methods.

Most of the physical molecular-weight determinations can be made only on the substance in solution. All these methods, which are described below, present difficulties and pitfalls, not the least of which is the relationship *presumed* to hold between the property being measured and the molecular weight. Practically all the equations from which the molecular weight is ultimately calculated are simplified versions of much more complicated rigorous forms, which either are not known or cannot be

used for lack of complete data or information. In still other instances, they are entirely empirical. All the equations have the common property of being more applicable in dilute solutions. Frequently an equation holds only in solutions so dilute that accurate measurement becomes impossible. Therefore, in careful work the molecular weight is determined at several concentrations and the correct value obtained by extrapolating to infinite dilution.

The agreement that may be expected from various methods is indicated in Table 6-2.

TABLE 6-2. MOLECULAR WEIGHT OF A FRACTIONATED ω -HYDROXYDECANOIC ACID POLYMER*

Method	M.W.
End-group titration.....	25,200
Sedimentation equilibrium.....	27,000
Diffusion coefficient alone, assuming spherical molecules...	2,400,000
Sedimentation velocity alone, assuming spherical molecules.	7,600
Diffusion plus sedimentation velocity†.....	52,000
Viscosity, assuming Staudinger's equation.....	31,000

* KRAEMER, E. O., and W. D. LANSING, *J. Am. Chem. Soc.*, **55**, 4319 (1933).

† High value probably because frictional coefficient was not the same for sedimentation and diffusion at the concentrations used.

Most of the physical methods may be divided into equilibrium and kinetic methods. Since the former, such as osmotic-pressure determination, are based upon the properties of the system at equilibrium, the equations can theoretically be derived from thermodynamics although mathematical complexities often force the use of simplified relations applicable at infinite dilution. The molecular weight as determined by an equilibrium method is independent of the shape or flexibility of the molecule.

Kinetic methods, such as viscosity determination, are based upon the properties of the system while the molecules are in motion. As a consequence, the derivations of the equations are on a less certain foundation. Usually, calibration of the method and evaluation of the constants depends upon comparison with an equilibrium method. Furthermore, the shape and flexibility of the molecules often have an important influence on the result.

617. Definitions of Molecular Weight. The concept of molecular weight presents little difficulty so long as low-molecular-weight pure substances are dealt with. But, in solution, complications may arise even with low-molecular-weight solutes. For example, consider benzoic acid dissolved in benzene. In concentrated solutions, it associates into double molecules via hydrogen bonding at the carboxyl group [structure (2-C), page 35]. As the solution is diluted, the double molecules dissociate, the dissociation becoming complete at infinite dilution.

Benzoic acid does not undergo similar association in water, where the hydrogen bonding takes place instead between the carboxyl groups and water molecules. An analogous state of affairs often exists in high-polymer solutions, and one would expect a polar solute, such as cellulose acetate, to exhibit considerably greater association in a solvent of low polarity than in one of high polarity. In order to eliminate this effect it is advisable to perform measurements in at least two solvents of differing polarity, to carry out the measurements at as low concentrations as possible, and to extrapolate the results to infinite dilution. In some cases, it is further advisable to make measurements at two different temperatures because increase in temperature decreases association.

The greatest complication in measurements on high polymers is the presence of molecules of different sizes, as a consequence of which an average molecular weight is obtained. Each method of investigation yields a particular type of average. With a single molecular-weight species all these "averages" assume the same value; but, the greater the polymolecularity, the greater the disparity among them.

The two most important types of average molecular weights, the number average and weight average, have already been defined (Sec. 108). These will nevertheless be reviewed here and compared with two additional types of averages.

✓ Number-average molecular weight is the ordinary average molecular weight usually meant and is defined by

$$\bar{M}_n = \frac{\text{total mass}}{\text{total no. of moles}} = \frac{m}{n}$$

It is the average given by methods that count molecules, such as end-group analysis and osmotic methods.

$$\bar{M}_n = \frac{n_1 M_1 + n_2 M_2 + \cdots}{n_1 + n_2 + \cdots} = \frac{\sum n_i M_i}{\sum n_i} = \sum N_i M_i$$

✓ Weight-average molecular weight is given by methods that depend on the weights of molecules present, such as light scattering and sedimentation equilibrium under certain conditions of measurement.

$$\bar{M}_w = \frac{m_1 M_1 + m_2 M_2 + \cdots}{m_1 + m_2 + \cdots} = \sum w_i M_i = \frac{\sum n_i M_i^2}{\sum n_i M_i}$$

The *z*-average molecular weight is obtained by sedimentation equilibrium under other conditions of measurement and is defined by

$$\bar{M}_z = \frac{\sum n_i M_i^3}{\sum n_i M_i^2}$$

Viscosity-average molecular weight is derived from viscosity measurements,

$$\bar{M}_v = \left(\frac{m_1 M_1^a + m_2 M_2^a + \dots}{m_1 + m_2 + \dots} \right)^{1/a} = \left(\sum w_i M_i^a \right)^{1/a} = \left(\frac{\sum n_i M_i^{a+1}}{\sum n_i M_i} \right)^{1/a}$$

where a is a constant depending upon the polymer-solvent system [Eq. (6-50)]. When a equals unity, the viscosity average reduces to the weight average.

Table 6-3 compares these various molecular-weight averages calculated for mixtures of two truly homogeneous substances.

TABLE 6-3. COMPARISON OF MOLECULAR-WEIGHT VALUES
(Calculated for hypothetical mixtures of two truly homogeneous substances with molecular weights of 20,000 and 80,000, respectively)

	Equal weights of each $m_A = m_B$ or $w_A = w_B = 0.5$ $N_A = 0.8, N_B = 0.2$	Equal moles of each $n_A = n_B$ or $N_A = N_B = 0.5$ $w_A = 0.2, w_B = 0.8$
Number average, \bar{M}_n ...	32,000	50,000
Viscosity average, \bar{M}_v ($a = 0.5$).....	45,000	64,800
Weight average, \bar{M}_w ($= \bar{M}_v, a = 1$).....	50,000	68,000
Viscosity average, \bar{M}_i ($a = 1.5$).....	54,510	70,370
z average, \bar{M}_z	68,000	76,470

Since various methods yield different types of averages, it follows that, if different molecular-weight methods are to be compared on a valid basis, it is essential to know the distribution of molecular sizes in the sample. Since this is usually not available, being tedious as well as not very precise of determination, the methods are generally compared by making measurements on fractionated material. The latter approach has its own pitfalls, as discussed in Sec. 614. Other sources of disagreement arise from the use of different solvents (see above) and the variable effects of shape and flexibility of the molecule on the results.

618. Osmotic Methods. The osmotic pressure, vapor-pressure lowering, boiling-point elevation, and freezing-point depression of a solution are all interrelated and indeed are different aspects of the same phenomenon. Historically, van't Hoff first proved this interrelationship by thermodynamic reasoning. Because he gave special prominence to the osmotic-pressure law, these four properties have come to be termed, collectively, *osmotic properties*. They are also termed *thermodynamic properties*.

The four exact equations for these properties, assuming that the perfect-gas law holds for the vapors, are

Vapor-pressure depression law. See Eq. (6-12a). $\phi_A = a_A p_A^0$, $p_s = a_s p_s^0$

Freezing-point depression law. See Eq. (6-18).

Boiling-point elevation law.

$$\frac{1}{T_b} - \frac{1}{T} = - \frac{R}{\Delta \bar{H}_{b,A}} \ln a_A \quad (6-27)$$

Where $\Delta \bar{H}_{b,A}$ is the partial molal heat of vaporization of the solvent:

Osmotic-pressure law.

$$\pi = - \frac{RT}{\bar{V}_{M,A}} \ln a_A \quad (6-28)$$

The osmotic properties of a solution are determined by the molar concentration so that the measurement of any one of these properties may be used as a method of molecular-weight determination. Indeed, practically speaking, the osmotic methods are the sole methods available for low-molecular-weight substances. The determinations are made in very dilute solution; and, in such case, the above equations reduce to

Vapor-pressure depression. See Eq. (6-7).

Freezing-point depression. See Eq. (6-19).

Boiling-point elevation.

$$\Delta t_b = K_{b,A} C = \frac{K_{b,A}}{M_s} c \quad (6-29)$$

Osmotic pressure.

$$\pi = CRT = \frac{RT}{M_s} c \quad (6-30)$$

The last equation is known as the *van't Hoff law*.

All four methods can be and have been used on low-molecular-weight materials. The more important relative advantages and disadvantages are as follows:

1. The freezing-point method may be used only at one temperature, the freezing point of the solvent. Although the boiling-point method may theoretically be used over a range of temperatures by controlling the pressure, such control is cumbersome and this method also is used only at one temperature, the normal boiling point of the solvent.

2. The boiling-point elevation is usually smaller than the freezing-point depression; furthermore, decomposition is more likely to occur at the elevated temperature.

3. The vapor-pressure depression is also small, and minute pressure changes are more difficult to measure than minute temperature changes.

4. The osmotic pressure is embarrassingly large, and the preparation of suitable semipermeable membranes is difficult.

A variation of the vapor-pressure depression method, known as the *isopiestic method*, has been found of great value. Using the same solvent, vessels containing solutions of the material being measured and a known material are kept close to each other in an evacuated chamber. Distillation occurs until the two solutions have the same vapor pressure. Another scheme is to place a droplet of the known and of the unknown, separated by an air bubble, into a capillary and determine the direction of the distillation by a microscope.

For high-molecular-weight materials, the first three of the above-listed relative advantages and disadvantages still obtain. However, the disadvantages of the fourth method turn into advantages, *viz.*, the osmotic pressures fall within the range of convenient and accurate measurement, and the preparation of suitable semipermeable membranes is much easier than for small molecules. Furthermore, although low-molecular-weight contaminants markedly affect all the osmotic methods, the very low molecular weight impurities do not interfere so much in the osmotic-pressure method as in the other methods, for such impurities diffuse through the membrane so that their effect cancels. (However, the Donnan equilibrium introduces difficulties in the case of ionic large molecules having low-molecular-weight electrolytic contaminants.)

The range of usefulness of the osmotic methods depends upon conditions. Most of the measurements on high polymers have been made with the freezing-point and the osmotic-pressure methods. In general, without using too elaborate equipment or precautions, the freezing-point method is convenient for the determination of molecular weights of low polymers, the upper limit being about 10,000, while the osmotic-pressure method is best suited for high polymers, the range being about 10,000 to 1,000,000.

As stated above, molecular-weight determinations of low-molecular-weight substances are made in dilute solution to achieve perfect behavior. Owing to assumptions made in the derivations, the equations listed above for the osmotic properties apply only in dilute solution. Indeed, as has already been stated, only an infinitely dilute high-polymer solution is sufficiently dilute for application of the ordinary thermodynamic equations applicable to small molecules. It is therefore essential to be able to extrapolate osmotic data accurately to infinite dilution. Experiment and theory have shown that Eq. (6-30) should be replaced by

$$\frac{\pi}{c} = \frac{RT}{M_s} + Bc \quad (6-31)$$

where B is a constant, depending upon the polymer-solvent system, which

is usually determined empirically but can be calculated from other properties, especially μ_s (Sec. 611). Consequently, to extrapolate to infinite dilution, π/c should be plotted against c . Similarly, $\Delta t/c$ of Eq. (6-19) is a linear function of concentration for polymer solutes.

The environment has a marked effect on osmotic properties. This is illustrated in Fig. 6-12, which shows the variation of π/c with c for solutions of polyisobutylene in two cyclic hydrocarbon solvents, cyclohexane and benzene. (The ordinate is the change in π/c from its value

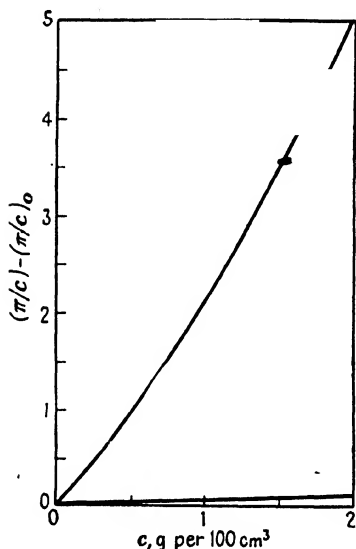


FIG. 6-12. Deviation from the van't Hoff law as a function of concentration in solutions of polyisobutylene in cyclohexane (upper curve) and benzene (lower curve). [P. J. Flory, *J. Am. Chem. Soc.*, **65**, 372 (1943).]

at infinite dilution.) Whereas there is a remarkable difference in the deviations from ideality in the two solvents, the values of π/c obtained by extrapolation to infinite dilution are nevertheless identical.

619. Diffusion and Sedimentation

Methods. The diffusion of molecules as well as other particles is a well-known phenomenon that manifests itself in many effects. As the Brownian movement indicates, this diffusion is by no means orderly but it is none the less sure. The term *diffusion pressure* is sometimes used to characterize the tendency of particles to move from regions of high concentration to those of lower concentration. Because the diffusion of particles depends upon their size, diffusion phenomena may be utilized for molecular-weight measurements.

The action of gravity on a mixture tends to cause segregation, the heavier particles settling to the bottom. Diffusion tends to offset the force of gravity. For particles in the colloidal realm (10 to 2,000 Å) and smaller, diffusion is the greater so that settling does not take place in a gravitational field. By using centrifugal methods it is possible to obtain forces many times gravity and thus cause colloidal and even smaller particles to settle out despite the diffusion pressure. The very high speed centrifuges required for this purpose are termed *ultracentrifuges*. The sensitivity of centrifugal methods increases with increase in particle size.

Ultracentrifuges are employed in two ways for the determination of particle sizes, (1) measurement in the early stages of sedimentation of the

rate of fall of the boundary separating the solution from the pure solvent (sedimentation-velocity method), and (2) determination of the concentration distribution of the particles when the rates of diffusion and sedimentation are equal (sedimentation-equilibrium method). The former method requires very large centrifugal forces (10,000 to 1,000,000 times gravity), and an analysis takes several hours. The greater the centrifugal force, the greater the amount of sedimentation that can take place before diffusion effects become disturbing. The latter method requires smaller centrifugal forces (1,000 to 100,000 times gravity), but a number of days of continuous operation is required to achieve equilibrium. Optical methods such as refractive index or light absorption are used as methods of observation. It is necessary that the particles be far enough from the bounding surfaces of the liquid so that surface concentration effects will be absent.

For diffusion and sedimentation measurements, it is desirable that the particles be very closely fractionated and be either all of the same molecular weight or divided into a few groups with widely different molecular weights. In systems containing particles distributed over a graded range of sizes, determination of molecular weights is uncertain although information on the distribution of the molecular sizes may be obtained.

Svedberg first derived mathematical equations for the calculation of the molecular weights of particles from their sedimentation characteristics. These equations apply only to dilute solutions of electrically neutral particles which are large in comparison with those of the solvent medium.

620. Diffusion- and Sedimentation-velocity Analysis. The primary object of measurement in diffusion studies is the diffusion constant D , which is the specific diffusion rate (amount of solute diffusing in unit time across unit area under unit concentration gradient). For particles which are large in comparison with those of the medium,

$$D_0 = \frac{RT}{f} \quad (6-32)$$

where D_0 is the diffusion constant at zero concentration, obtained by plotting D against c and extrapolating to infinite dilution, and f is the frictional coefficient per mole of particles. For spherical particles, Stokes's law is

$$f_s = 6\pi\eta N_0 r = 6\pi\eta N_0 \left(\frac{3Mv}{4\pi N_0} \right)^{1/3} \quad (6-33)$$

where η is the absolute viscosity of the medium, N_0 Avogadro's number, r the radius of the particles, and v the specific volume of the particles.

The primary object of measurement in the sedimentation-velocity

method is the sedimentation constant s .

$$s = \frac{u}{\omega^2 l} \quad (6-34)$$

where u is the velocity of fall of the boundary separating solute from supernatant liquid, ω the angular velocity, and l the distance of the boundary from the axis of rotation.

The fundamental equation of the sedimentation-velocity method is

$$s_0 = \frac{M(1 - v\rho)}{f} \quad (6-35)$$

where s_0 is the sedimentation constant at zero concentration, obtained by plotting $1/s$ against c , v the specific volume of the particles (strictly, the partial specific volume), ρ the density of the solution, and f the molar frictional coefficient. For spherical particles f is given by Eq. (6-33).

It is evident that, if the particles are known to be spherical, measurement of either diffusion constants or sedimentation constants leads directly to size and molecular weight, the frictional coefficient being calculated by Eq. (6-33).

For shapes other than spherical, which is the case for most high polymers, both the diffusion constant and the sedimentation constant must be measured in order to eliminate the frictional coefficient. Combining Eqs. (6-32) and (6-35),

$$M = \frac{s_0 RT}{D_0(1 - v\rho)} \quad (6-36)$$

Table 6-2 illustrates the error in using either the diffusion constant or the sedimentation constant for calculation of molecular weight when the particle is nonspherical; this table also indicates the result of combining the two measurements.

These methods are not well suited for unfractionated polymers, not only because the experimental data are less accurate, but also because the nature of the average is affected by the methods of measurement and by the shape and flexibility of the molecules. In general, weight-average molecular weight is obtained.

621. Sedimentation-equilibrium Analysis. In this method, the variation of concentration with depth is determined after the system has achieved equilibrium. The molecular weight is calculated by the equation

$$M = \frac{2RT \ln(c_2/c_1)}{(1 - v\rho)\omega^2(l_2^2 - l_1^2)} \quad (6-37)$$

where c_1 and c_2 are the concentrations of particles at depths l_1 and l_2 ,

respectively. (Theoretically, activities should be used instead of concentrations, although in most cases the correction is small.)

This method is satisfactory for an unfractionated polymer and in such case the molecular-weight average obtained depends upon the experimental method of observation. If the variation of concentration with depth is determined by light absorption, the formula yields the weight average. If the variation of concentration with depth is determined by refractive index (the so-called "scale optical method"), the formula yields the z average (Sec. 617).

622. Viscosity Methods. Slight changes in high-polymer systems have considerable effects on viscosity. Since viscosity is relatively easy to measure precisely, many viscosity researches have been carried out on high polymers. In the course of this work, several methods have been developed that are suitable for the measurement of a very broad range of molecular weights. However, since the equations contain empirical constants that must be obtained by measurements on polymers of known molecular weights determined in some other way, viscosity measurement cannot be called an absolute method for molecular-weight determination.

623. Viscosity of Melts. Some simple relationships have been found between viscosity and molecular weight for molten low polymers. The materials must usually be well above the melting points, probably because of the presence of crystal nuclei near the melting point. One of these relationships is

$$\log \eta = c + dM \quad (6-38)$$

where η is the viscosity (absolute, kinematic, Saybolt, or other viscosity depending on the polymer type) and c and d are constants characteristic of the polymer type and temperature. This equation usually holds for homologous series of low-molecular-weight nonpolar compounds, *e.g.*, the aliphatic linear hydrocarbons, ethers, and esters. In these cases the equation shows deviations at higher molecular weights, *e.g.*, for the esters when the molecular weight is above 300. The relationship holds for at least one type of polymer, the polyethylene glycols (Fig. 6-13). In this case, the particular molecular-weight average used makes little difference owing to the narrow size distribution (Fig. 4-7, page 125).

A second relationship is

$$\log \eta = C + DM^{1/2} \quad (6-39)$$

where C and D are constants depending on the polymer type and temperature. This equation holds for at least one series of low-molecular-weight compounds, the cyclic dimethylsiloxanes. It has also been established for several series of low polymers such as linear polyesters with molecular weights up to 10,000, M being the weight-average molec-

ular weight, and linear dimethylsiloxanes in the range 2,500 to 150,000, for which M is the number-average molecular weight. [In the latter case neither Eq. (6-38) nor (6-39) applies for values of M below 2,500.]

The above equations afford an accurate means for determining the molecular weights of low polymers but cannot be developed for high

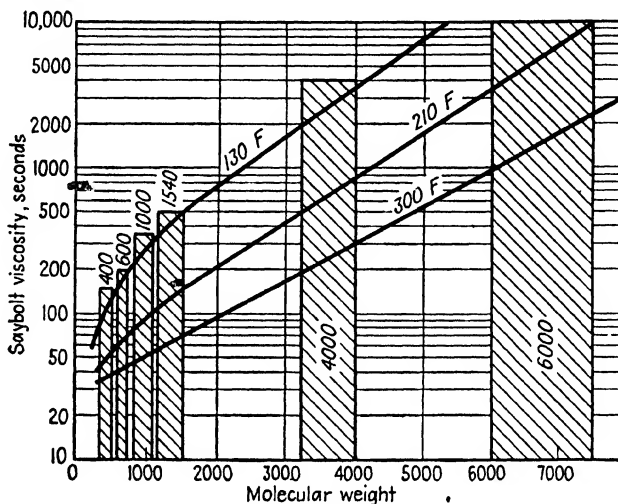


FIG. 6-13. Viscosity as a function of molecular weight for the polyethylene glycols. [C. P. McClelland and R. L. Bateman, *Chem. Eng. News*, **23**, 247 (1945). Courtesy of Carbide and Carbon Chemicals Corp.]

polymers since the latter usually decompose before they become mobile liquids.

624. Viscosity of Suspensions. Particles suspended in a liquid medium block the motion of the molecules of the solvent and produce an increase in viscosity. Einstein was the first to make a theoretical hydrodynamic analysis of such systems. For very dilute suspensions of *spherical* particles whose size is large relative to that of the solvent molecules, the Einstein equation is

$$\eta_r = \frac{\eta}{\eta_0} = 1 + \frac{5}{2} V_s \quad (6-40a)$$

Also,

$$\eta_{sp} = \eta_r - 1 = \frac{5}{2} V_s \quad (6-40b)$$

where η is the absolute viscosity of the solution, η_0 is the absolute viscosity of the pure solvent, η_r equals η/η_0 , the relative viscosity (by definition), η_{sp} equals $\eta_r - 1$, the specific viscosity (by definition), and V_s is the volume fraction of particles in the solution.

This equation has been widely tested and confirmed. With increase in concentration a correction is necessary for the mutual interference of the particles. Thus, for concentrated suspensions of spherical particles the following equation applies:

$$\eta_r = \left\{ 1 + \frac{5V_s}{4[1 - (V_s/b)]} \right\}^2 \quad (6-41)$$

where b is a function of the size distribution, being 0.74 for uniform size. These equations are not very useful for solutions of high polymers, for the molecules are more often linear than spherical. However, the relations are applicable to many colloidal dispersions, for example, rubber latices, in which the particles are essentially spherical.

Suspensions of rodlike particles have been treated theoretically by several authors; but, owing to various complications, no single equation is generally applicable, a number of equations having resulted to cover different cases. Thus, for very dilute suspensions of *rigid* particles which are flowing so slowly that the Brownian movement overcomes any orientation that might result from flow, Simha has derived the following:

For rods,

$$\frac{\eta_{sp}}{V_s} = \frac{f^2}{15 \ln 2f - (4\frac{5}{2})} + \frac{f^2}{5 \ln 2f - (5\frac{1}{2})} + \frac{14}{15} \quad (6-42a)$$

and for disks,

$$\frac{\eta_{sp}}{V_s} = \frac{16}{15} \frac{f}{\tan^{-1} f} \quad (6-42b)$$

where f is the axial ratio of the particles.

Equations of the above type have been tested in a few cases where rodlike particles such as cut fibers have been suspended in a liquid medium. General agreement has been observed. However, they do not apply to thin, flexible particles such as dissolved chain molecules, either theoretically or experimentally. Hence, they are not useful for high-polymer studies. It should also be noted that in equations of this type increase in viscosity depends only on the total volume of the solute and is independent of particle-size distribution. Consequently, they cannot be used for particle-size determination.

625. The Viscosity of High-polymer Solutions. The viscosity relations of high-polymer solutions are more complicated than those of suspensions of rigid particles. Relations such as Eqs. (6-40) and (6-42) are limited to rigid particles and, what is more, do not take into account forces of attraction between the solvent and the dispersed particles. High-polymer chains in solution whip about and wriggle, exhibiting external movement of the molecule as a whole and internal movement of the

individual segments. Furthermore, the chain segments are of molecular dimensions so that the forces of attraction between solute and solvent cannot possibly be neglected.

It is, then, not surprising that the viscosity in solution is always considerably higher than that predicted by the Einstein and related equations, which apply for suspensions of particles only when the cross section of the latter are so much larger than molecular dimensions that the forces of attraction between dispersed particle and liquid medium may be overlooked. As pointed out in Sec. 315, the solution viscosity of chain polymers varies with the nature of solute and solvent and furthermore, for a given solute and solvent, with both the size and the shape of the solute molecule—the larger the solute molecule, the higher the viscosity; the more nearly spherical, the lower the viscosity.

The simplest relationships are obtained when one considers a particular solute-solvent combination in which the only factor allowed to vary is the length of the chain-polymer solute. Staudinger, working with polymers of relatively low molecular weights, discovered the following empirical rule:

$$\frac{\eta_{sp}}{c} = K_s \bar{M}_w \quad (6-43)$$

where η_{sp} is the specific viscosity, c the concentration, either in mer-moles of solute or mass of solute per unit volume of solution, K_s a specific constant for a particular polymer and solvent (often referred to as the Staudinger constant), and \bar{M}_w the weight-average molecular weight.

Staudinger and coworkers determined K_s values from the viscosities of solutions of polymers of molecular weights below 10,000 where cryoscopic methods could be used for independently determining molecular weights.

Viscosity is a relatively simple measurement to perform. Furthermore, contrary to the situation with osmotic measurements, increase in the molecular weight does not decrease precision of measurement. For these reasons, the Staudinger rule in its above form has been used extensively for determining and reporting molecular weights. Unfortunately, both theory and experiment indicate that the ratio η_{sp}/c is not constant, *i.e.*, not independent of concentration (Fig. 6-14). The ratio at infinite dilution is therefore used. This ratio is termed the *intrinsic viscosity* and is designated by the symbol $[\eta]$; that is,

$$[\eta] = \left(\frac{\eta_{sp}}{c} \right)_{c \rightarrow 0} \quad (6-44)$$

(Some authors have called the ratio η_{sp}/c the intrinsic viscosity regardless of concentration.) Staudinger's equation is therefore best written in its

more valid form,

$$[\eta] = K_s \bar{M}_w \quad (6-45)$$

However, even extrapolation to infinite dilution is not sufficient to eliminate shortcomings and limitations arising from the Staudinger rule since it has been demonstrated that the value of a Staudinger constant for a low polymer, even if extrapolated to infinite dilution, may not hold for the same species of polymer in high-molecular-weight ranges. In other words, different samples of a particular high polymer, *e.g.*, cellulose acetate, all dissolved in a particular solvent, *e.g.*, acetone, may have different Staudinger constants. It is unfortunate, therefore, that the literature contains so many molecular-weight values based on the Staudinger rule and Staudinger "constants." Many of these values are seriously in error. Owing to this uncertainty, high polymers are now frequently characterized by their intrinsic viscosities, the results not being converted into molecular weights.

Owing to the importance of the intrinsic viscosity both for itself and for calculating molecular weights with the Staudinger and other equations, it is essential to be able to extrapolate viscosity-concentration data accurately to infinite dilution. For this purpose it is highly desirable to have for any particular system a mathematical viscosity-concentration relation, preferably one that can be readily arranged for plotting as a straight line. A great many relations have been proposed, one of the simplest of which was discovered years ago by Arrhenius:

$$\frac{\ln \eta_r}{c} = \frac{2.303 \log \eta_r}{c} = k_A \quad (6-46)$$

where k_A is a specific constant for a particular sample of polymer solute dissolved in a particular solvent.

This equation is especially valuable in that not only is it a straight-line plot but also it holds well at higher concentrations. Thus, comparison of Figs. 6-14 and 6-15 shows that, for a variety of polymers, $(\ln \eta_r)/c$ is more nearly constant than η_{sp}/c . Furthermore, at infinite dilution, $(\ln \eta_r)/c$ is identical with the intrinsic viscosity $[\eta]$.

$$[\eta] = \left(\frac{\eta_{sp}}{c} \right)_{c \rightarrow 0} = \left(\frac{\eta_r - 1}{c} \right)_{c \rightarrow 0} = \left(\frac{\ln \eta_r}{c} \right)_{c \rightarrow 0}$$

A much more recent equation proposed by Martin is

$$\log \frac{\eta_{sp}}{c} = \log [\eta] + K [\eta]c \quad (6-47)$$

Huggins has shown that Eqs. (6-46) and (6-47), as well as most of the others which have been proposed, reduce to the following in dilute

solution:

$$\frac{\eta_{sp}}{c} = [\eta] + kc \quad (6-48a)$$

in which

$$k = k'[\eta]^2 \quad (6-48b)$$

where k' is a constant for a given solvent and species of high-polymer solute which often holds for all samples of the high-polymer regardless

of molecular-weight range. Equation (6-48) gives straight lines in dilute solution (Fig. 6-16).

Until recent years the weakness of the viscosity method as compared with the osmotic and diffusion methods has been the entirely empirical nature of the Staudinger and other equations. Kuhn and Huggins in various papers beginning in 1932 developed a number of theoretically grounded equations for homogeneous high-polymer chains of varying degrees of flexibility. These equations reduce to

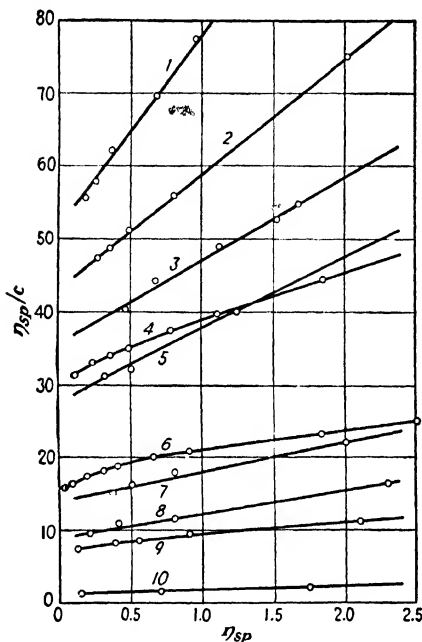
$$[\eta] = KM^a \quad (6-49)$$

They showed that the limits for the constant a should lie between 0.5 for perfectly flexible, randomly kinked polymer chains, *i.e.*, matted-coil molecules, and 2 for completely rigid rod-shaped molecules.

FIG. 6-14. Variation of η_{sp}/C in dilute high-polymer solutions. See Fig. 6-15 for key to curves. [A. R. Kemp and H. Peters, *Ind. Eng. Chem.*, **33**, 1263 (1941).]

molecules. Free-draining chains (Sec. 314) should have a value of a that is near 1. This equation has been verified experimentally for a number of carefully fractionated high polymers, the molecular weights in most cases having been determined by osmotic-pressure measurements.

As predicted by theory, the value of a increases with chain rigidity (Table 6-4, page 252). Thus, for amylose chains, which are among the most rigid linear polymers thus far encountered, a has a value of 1.5. Furthermore, it has been found that change in the temperature employed in polymerizing the solute chains may change the value of a considerably, probably corresponding to a change in rigidity or structure. It has also been found that in one case in which Eq. (6-49) did not hold, the constant



a apparently decreasing with increasing molecular weight, the amount of folding was probably greater in the higher molecular-weight range. These results are interesting and indicate that the constant a is of value in structure elucidation.

Since most high polymers are not homogeneous, the nature of the "average" molecular weight yielded by this equation is of considerable importance. Flory has shown that, more generally,

$$[\eta] = K_F \bar{M}_v^a \quad (6-50)$$

\bar{M}_v is the viscosity-average molecular weight.

The final word has probably not yet been said on the viscosity-molecular-weight relationship. At the present writing, Eqs. (6-49) and (6-50) represent our best knowledge of the subject, although there are indications that an equation with another term is necessary in some cases, *viz.*,

$$[\eta] = KM^a + K'M^{2a} \quad (6-51)$$

in which K' is very much smaller than K so that the second term is significant only in the very high molecular-weight range.

626. Optical Methods. If a beam of light traverses an absolutely uniform transparent region, such as a vacuum or perfectly crystalline optical quartz, no lateral radiation takes place. In other "homogeneous regions," *e.g.*, gases and liquids, the thermal motions produce momentary fluctuations in density, which in turn cause local variations in index of refraction and thus result in scattering of some of the light. The short wave lengths are affected more than the long so that the scattered light is "bluer" than the incident light. (This effect accounts for the blue color of the sky.) This scattering produces a turbidity in the medium, and it has been found that the turbidity observed agrees well with that predicted by a theoretical treatment.

If a solute or very fine suspension is added to the medium, fluctuations in concentration are superposed on the fluctuations in density of the liquid. The magnitude of this effect depends upon the size of the

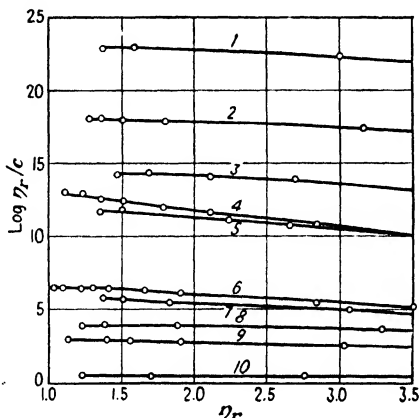


FIG. 6-15. Variation of $\log \eta_r/C$ in dilute high-polymer solutions. Curve 1: rubber in chloroform. Curve 2: rubber in hexane. Curve 3: polyisobutylene in hexane. Curve 4: polystyrene in benzene. Curve 5: rubber in hexane. Curve 6: polyester of ω -hydroxyundecanoic acid in chloroform. Curve 7: gutta-percha hydrocarbon in benzene. Curve 8: masticated rubber in hexane. Curve 9: polystyrene in benzene. Curve 10: depolymerized rubber in hexane. [A. R. Kemp and H. Peters, *Ind. Eng. Chem.*, **33**, 1263 (1941).]

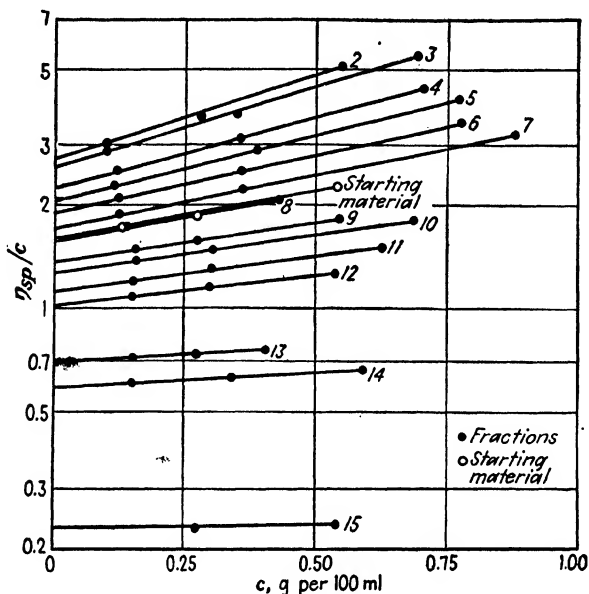


FIG. 6-16. Viscosity-concentration relation of original and fractionated cellulose acetate samples in acetone. [A. M. Sookne and M. Harris, *Ind. Eng. Chem.*, **37**, 475 (1945).]

TABLE 6-4. VISCOSITY—MOLECULAR-WEIGHT RELATIONSHIPS

$$\text{Equation: } [\eta] = KM^a$$

System	$K \times 10^4$	a
Poly-ε-amino caprolactam in 40% H_2SO_4	24.	0.51
Polystyrene in butanone, 40 C.....	7.0	0.53
Polystyrene in toluene, 30 C.....	3.7	0.62
Polyisobutylene in diisobutylene, 20 C.....	3.60	0.64
Polydimethylsilicone in toluene.....	2.	0.66
Butadiene-styrene copolymer in toluene, 30 C.....	5.4	0.66
Hevea rubber in toluene.....	5.02	0.67
Polyvinyl alcohol in water, 50 C.....	5.9	0.67
Polyvinyl acetate in acetone, 50 C.....	2.8	0.67
Polymethylmethacrylate in benzene, 25 C.....	0.94	0.76
Cellulose in cuprammonium hydroxide, 25 C.....	0.85	0.81
Polymethylmethacrylate in chloroform, 20 C.....	0.49	0.82
Cellulose acetate in acetone, 25 C.....	1.49	0.82
Cellulose acetate-butyrate in acetone, 25 C.....	1.37	0.83
ω-Polyhydroxyundecanoic acid in chloroform, 25 C.....	0.32	1.0
Pectinic acid in 0.155 M NaCl solution, 25 C.....	0.014	1.34
Amylose in ethylenediamine.....	1.5

particles. Thus, the blue color of a thin layer of tobacco-smoke particles is as intense as the blue color of the sky, which is produced by a layer of air equivalent to a depth of 5 miles at atmospheric pressure. The scattered light is plane-polarized. This scattering is known as the *Tyndall effect*. To produce pure scattering effects, the dispersed particles must be no longer than one-tenth the wave length of the light. (With larger particles, such as dust motes, some light is reflected and refracted in the usual manner, no change in wave length occurring; hence this scattered light is not polarized.)

Owing to this scattering the intensity of the light traversing a solution decreases with distance.

$$I = I_0 e^{-\tau l} \quad (6-52)$$

where I_0 and I are the intensities of the light entering and leaving the cell, τ is the turbidity of the solution, and l is the length of the cell. The turbidity can also, and indeed more conveniently, be obtained by measuring the intensity of the light scattered in directions off the primary beam.

Debye has shown that the turbidity of polymer solutions is closely connected with the molecular weight of the dissolved macromolecules. The equation, derived from the classical theory of light, is

$$H \frac{c}{\tau} = \frac{1}{M} + \frac{2B}{RT} c \quad (6-53)$$

where H is a constant for any particular polymer-solvent system, calculated from certain measured properties of the system, such as refractive index, and B is a constant, usually determined empirically, but identical with B of Eq. (6-31). The molecular weight is obtained by plotting $H(c/\tau)$ against c and extrapolating to zero concentration (Fig. 6-17).

TABLE 6-5. MOLECULAR-WEIGHT DATA ON CELLULOSE ACETATE FRACTIONS

Fraction	Light scattering		O.P.	Viscosity (constants evaluated by O.P.)
	Uncorrected (see Fig. 6-17)	Corrected for depolarization and dissymmetry		
8B	118,000	173,000	163,000
23B	91,700	135,000	133,000	
18B	60,200	77,000	75,000
32B	47,200	60,000	65,000	

STEIN, R. S., and P. DORY, *J. Am. Chem. Soc.*, **68**, 159 (1946).

Various corrections are necessary for depolarization of the scattered light, and angular dependence of scattered light (dissymmetry). Com-

parison of molecular weights as determined by several methods is given in Table 6-5.

The light-scattering method theoretically gives weight-average molecular weight. However, for an unfractionated polymer, Eq. (6-53) does not hold well, the plot of $H(c/\tau)$ vs. c being slightly curved, so that extrapolation to zero concentration is more difficult. Moreover, the application of the above-mentioned corrections is less certain.

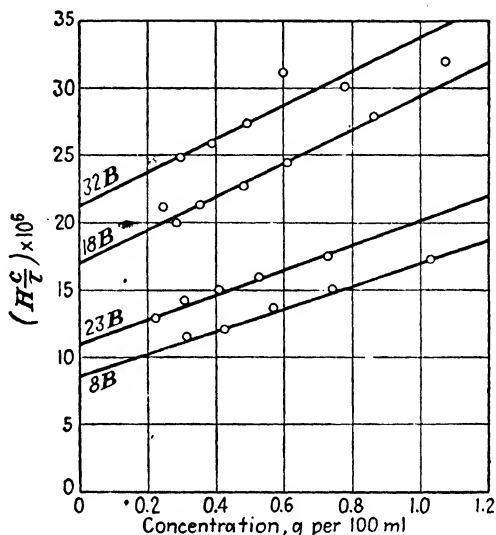


FIG. 6-17. Light scattering of cellulose acetate fractions. [R. S. Stein and P. Doty, *J. Am. Chem. Soc.*, **68**, 159 (1946).]

Interesting aspects of this method are that the precision of the results increases with increase in the molecular weight. Indeed, the lower limit for the method is molecular weights of 10,000, which represents the upper limit for ordinary cryoscopic measurements. Furthermore, this method may also be employed for establishing the shapes and flexibility of polymer molecules (Sec. 628).

627. Other Methods. Many other properties of high polymers are more or less exact functions of their molecular size; among them are melting point (Fig. 2-4, page 44), precipitability (Fig. 6-11, page 211), and, more roughly, tensile strength (Fig. 2-5, page 45) and electrical properties (Fig. 10-10, page 444). Such properties have been suggested as methods for molecular-weight determination but are of limited value, for any or all of the following reasons: unsure theoretical foundation, insensitivity to high degrees of polymerization, low precision, applicability to but a few types of high polymers, etc. These functions, however, are frequently suitable and useful for the calculation of physical properties from the degree of polymerization.

SHAPES OF HIGH-POLYMER MOLECULES

628. The shapes of high-polymer molecules are less readily determined than their sizes. Indeed, the determination of the shape usually requires measurement of size as well.

Using the value of molecular weight (as determined by the sedimentation equilibrium or osmotic methods) and the value of the sedimentation constant from Eq. (6-35) permits the calculation of f , the frictional coefficient. Comparison of this value of f with the value for spherical particles [Eq. (6-33)] indicates whether the particle is spherical and, if not, the deviation from spherical symmetry. It should be noted that this method gives the shape of the *solvated* particle.

As stated previously, the more compact the structure of a molecule, the lower its viscosity. Assume that it is desired to determine the relative degree of branching of a high polymer prepared by different methods. The materials are first fractionated and the molecular weights of the individual fractions determined by osmotic or other methods into which the shape of the molecule does not enter. Then the viscosities of fractions of the same molecular weight are measured and the viscosity molecular weights calculated. The ratio of the two molecular weights is a measure of the degree of branching; the nearer the value of the ratio is to unity, the more linear the molecule (Table 6-6).

TABLE 6-6. SHAPES OF RUBBER MOLECULES

Polymer	M.W. (osmotic)	$\frac{M \text{ (Osmotic)}}{\bar{M} \text{ (Viscometric)}}$
Insoluble:		
Butadiene.....	920,000	54.2
Buta S.....	840,000	26.4
Difficultly soluble:		
Buta S.....	650,000	13.1
Soluble:		
Hevea rubber.....	404,000	3.37
Buta S.....	350,000	6.8
Neoprene.....	123,000	6.65
Butadiene-methyl methacrylate.....	116,000	2.26

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The most useful method of investigating shapes and flexibility of polymer molecules is by light scattering. As already stated, for the calculation of molecular weights, corrections are necessary for the depolarization of the scattered light and for dissymmetry. These phenomena are connected with the shape and flexibility of the polymer molecules.

Another method of ascertaining shape and flexibility is by streaming birefringence. If a solution of polymer molecules is subjected to shear, the molecules are aligned and the system becomes anisotropic, exhibiting birefringence between crossed polarizers. In principle, the method permits the determination of the average effective axis ratio and its change with concentration and rate of shear.

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CHAPTER 7

RHEOLOGY

GENERAL CONSIDERATIONS

700. When a body in any physical state is subjected to an external stress, it is deformed. That property of the body by virtue of which it tends to resist deformation is called its *consistency*. There are two basic types of deformation, *elastic deformation*, which is temporary and disappears upon release of the stress, and *flow*, which is a permanent deformation. Rheology is the study of the deformation and flow of matter. Its fundamental goal is to describe the mechanical behavior of a material in terms of the three variables, stress, strain, and time.

When a deformation takes place, it means that particles within the body have moved with respect to one another. The particles in question may be single atoms, ions, molecules, crystals or other molecular aggregates, or mers of macromolecules. If a permanent deformation (flow) takes place, regardless of whether the body has been stretched, compressed, bent, twisted, dented, or torn, this means that particles within the body have slipped permanently past one another against the restraining action of interparticle forces of attraction. Such slippage is what we call *shear*. It follows that the study of the strength of materials resolves itself into a determination of their rheological characteristics.

701. Ideal Elastic Deformation. Hookian Solids. An *ideal elastic deformation* is one that takes place instantaneously on application and disappears completely and instantaneously on release of the deforming stress. In other words, in an ideally elastic body there is no time lapse between application of stress and assumption of final shape; the strain is independent of time and is a function of stress only.

In 1676 Hooke showed that, *for small strains*, certain solids exhibit ideal elasticity and the stress is directly proportional to the strain. In accordance with Hooke's law,

$$\frac{s}{\epsilon} = E = \text{constant} \qquad \frac{\Delta l}{l} = \frac{s}{E} \qquad (7-1)$$

where s is the applied stress (tension or compression) in force per unit cross-sectional area, l the original length, ϵ ($= \Delta l/l$) the axial strain, and E Young's modulus of elasticity in tension or compression.

The variation of strain with time under a constant stress is called the *flow curve*. The flow curve and stress-strain curve for a Hookian ideally elastic body are shown in Fig. 7-1. By mechanical analogy, the rheological behavior of a Hookian ideally elastic body is that of a steel spring. A body or any part of a body showing such behavior will hereinafter be called an *ideally elastic element*. Hooke's law holds for strains usually no greater than about 0.1 per cent.

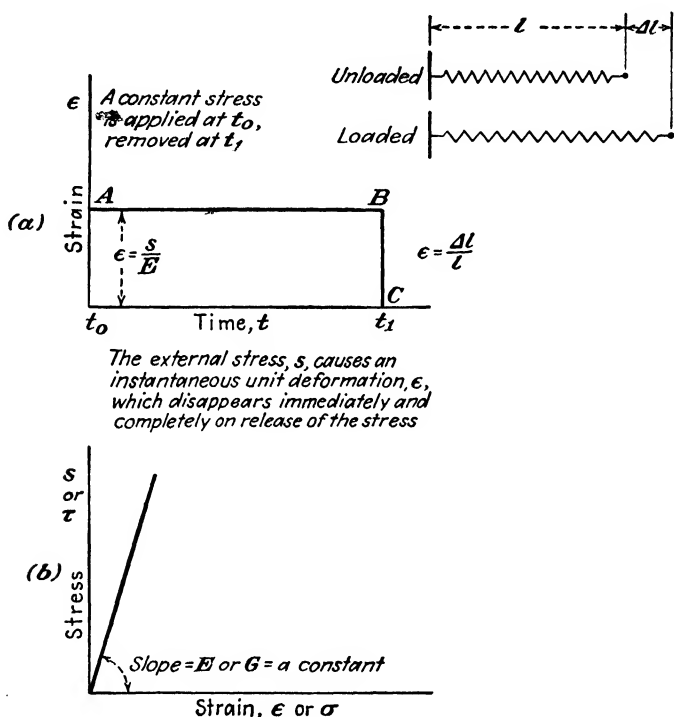


FIG. 7-1. Hookian ideal elastic deformation.

If the stress on a solid is increased to a sufficiently high value called the *yield value*, permanent deformation (flow) can be induced. On release of the stress the solid no longer returns to its original dimensions but has suffered a permanent set. In other words, above the yield value the solid is no longer behaving as an elastic body. Rheologically, a solid is defined as a body possessing a finite yield value. This distinguishes it from a fluid, for which the yield value is zero.

A unit elongation ϵ is always accompanied by a lateral unit contraction in dimension, q , which, for small strains, is also proportional to the stress. The ratio q/ϵ is called *Poisson's ratio* and is usually designated by the symbol μ . If the density of the material remains unchanged under stress,

$\mu = 0.5$. If the material decreases in volume, $\mu > 0.5$; if it expands under stress, $\mu < 0.5$.

If, instead of being stretched, a solid is deformed by a shearing stress (Fig. 7-2), the extent of deformation is conveniently expressed by

$$\tan \alpha = \sigma = \frac{\Delta x}{y} \quad (7-2)$$

For a Hookian solid, the shear strain σ is proportional to the shear stress τ , so that

$$\frac{\tau}{\sigma} = G = \text{modulus of shear or rigidity} \quad (7-3)$$

The modulus of shear G is a characteristic of the material analogous

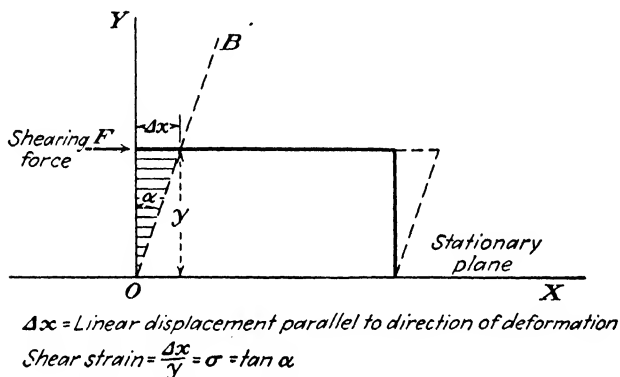


FIG. 7-2. Deformation of a solid under simple shear.

to E , the modulus of elasticity, and Eq. (7-3) is Hooke's law applied to shear (Fig. 7-1b).

If a body undergoes a pure compression owing to pressure uniformly applied on all surfaces, the elastic resistance is measured by the compressibility coefficient, $(1/V) (\partial V / \partial p) = \kappa$. It can be shown that for an isotropic body within the range of Hooke's law, the properties κ , E , G , and μ are related as follows:

$$E = \frac{3(1 - 2\mu)}{\kappa} = 2G(1 + \mu) \quad (7-4)$$

It follows from Eq. (7-4) that, if two of the fundamental constants are known, the others may be calculated. Any two are sufficient to characterize a material within the range of Hooke's law.

As previously mentioned, when no change in density accompanies deformation, $\mu = 0.5$. This is the situation in liquids, for the molecules

are so mobile that no change in volume occurs under stress. From this it follows that the term $1 - 2\mu$ must equal zero, so that E also equals zero or a liquid has no elasticity. Experimental values for μ usually range from 0.2 to 0.5, and it may be said that, the more nearly a material approaches a liquid, the closer the value of μ approaches 0.5 and the more nearly E equals $3G$. Poisson ratios of a few materials are given in Table 7-1.

TABLE 7-1. POISSON'S RATIO FOR VARIOUS MATERIALS

Material	Poisson's Ratio (Approximate)
Cast iron.....	0.17
Concrete.....	0.19
Glass.....	0.23
Steel.....	0.26
Aluminum.....	0.33
Copper.....	0.36
Hard rubber.....	0.39
Lead.....	0.40
Polystyrene.....	0.48
Soft rubber.....	0.49
Gelatin gel.....	0.50

702. Pure Viscous Flow; Newtonian, or Simple Liquids. Rheologically, a liquid differs from a solid in that it will deform (flow) under an infinitesimal stress; *the yield value is zero*. A liquid in a state of rest cannot support stresses other than hydrostatic pressure. Any other stress produces a continuously increasing deformation, none of which is recovered when the stress subsides. In a liquid, strain is a function not only of stress but of time as well.

Although the yield value is zero, there is in a liquid an internal frictional resistance to flow called the *viscosity*.

If the velocity of flow is not too great, the flow of a liquid is laminar. Layers of the liquid slip past one another in regular fashion, and a velocity gradient is established among them. For example, if a liquid flows not too rapidly through a pipe, the velocity is greatest at the center and zero at the walls. The effect is readily visualized by pressing the finger obliquely downward on a stack of new playing cards and observing the regularity of slip. The bottom card remains stationary, the top card travels farthest. Each card represents a liquid layer. This type of flow is called *viscous flow*.¹

In 1685, Newton discovered that in many liquids in order to maintain

¹ At high velocities, the laminar character of the flow is destroyed owing to the appearance of swirls and eddies. This *turbulent*, or *hydraulic*, flow, although very important in engineering practice, is not considered here. It does not follow the same laws as viscous flow.

the motion of a given liquid plane at a constant velocity there must be exerted a shearing force F over an area A which is proportional to the velocity gradient. Figure 7-3 shows two liquid planes, each of area A , moving parallel to the flow a distance dy apart with a velocity difference dv . In terms of the figure, $F/A = \tau$ is the shearing stress and $dv/dy = D$ is the velocity gradient in the liquid. According to Newton's law,

$$\frac{\tau}{D} = \eta = \text{a constant} \quad (\text{temperature constant}) \quad (7-5a)$$

or

$$D = \frac{1}{\eta} \tau = \phi \tau \quad (\text{temperature constant}) \quad (7-5b)$$

where η is the coefficient of viscosity, or internal friction, and ϕ is the fluidity, the reciprocal of the viscosity.

The plot of Newton's law is shown in Fig. 7-4b. The flow of many real liquids such as water, benzene, and mercury follows this law. They are variously called *Newtonian*, *simple*, or *pure viscous* liquids. The D - τ curve is a straight line passing through the origin.

The slope of this straight line is the reciprocal of the viscosity. Hence, the steeper the slope, the *lower* the viscosity.

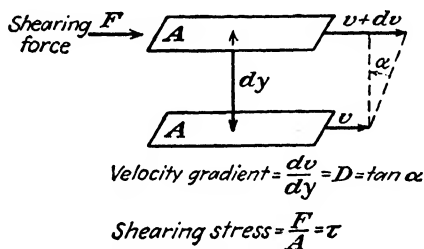


FIG. 7-3. Flow of a liquid under shear.

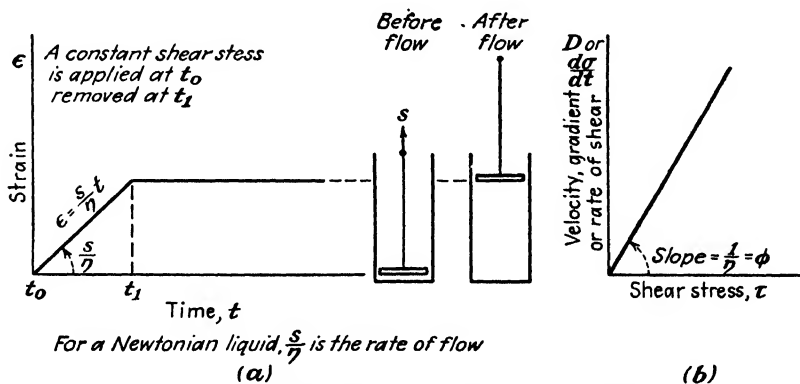


FIG. 7-4. Newtonian, pure viscous, or simple flow.

As previously stated, the viscosity of a liquid is the internal resistance against the slippage (shear) of one liquid plane past its neighbor under the conditions of laminar flow. If the coefficient of viscosity is high, the

resistance to flow is great; *i.e.*, the liquid is viscous. Hence we are accustomed to call the coefficient of viscosity merely the viscosity.¹

The rate of shear $d\sigma/dt$ is equivalent to the velocity gradient D . Hence the plot of rate of shear vs. shearing stress τ is the same as the D - τ curve (Fig. 7-4b). Since rate of flow is directly dependent on the velocity gradient and the shearing stress is the driving force or pressure, it is important to note that, in a Newtonian liquid, the viscosity is a constant which is independent of the rate of flow (without turbulence) or the driving force. Thus, Poiseuille's equation for the flow of liquid through a capillary is

$$\frac{V}{t} = \frac{1}{\eta} \left(\frac{\pi r^4 p}{8l} \right) \quad (7-6)^*$$

The plot of rate of flow V/t vs. driving pressure p is a straight line passing through the origin for a Newtonian liquid.

A Newtonian liquid is devoid of elasticity. By mechanical analogy its deformation under stress is represented by a weightless piston moving in a cylinder or dashpot filled with a medium that offers a certain resistance (Fig. 7-4a). For a Newtonian liquid, the amount of flow is a linear function of time, *i.e.*,

$$\epsilon = \frac{s}{\eta} t = \phi s t \quad (7-7)$$

A body or any part of a body showing such rheological behavior will be called a viscous element.

There are many liquids for which the D - τ curve is not a straight line (Fig. 7-23a). According to most rheologists it is not proper to apply the term viscosity to such liquids. One must speak of apparent viscosity, "viscosity," or consistency in such cases.

¹ Formally defined, after Maxwell, the viscosity of a liquid is measured by the tangential force on a unit area of either of two horizontal liquid planes, unit distance apart, required to move one plane with unit velocity with regard to the other plane, the space between being filled with the substance. The unit of viscosity is the poise, which is 1 dyne-sec per sq cm. A centipoise is 1/100 poise; for water at 20°C, η is 1.002 centipoises. The kinematic viscosity is η/ρ , the viscosity divided by the density, and its unit is the stoke. The fluidity ϕ is the reciprocal of the viscosity and is expressed in rhes. A rhe is 1/poise.

In English engineering dimensions, the unit of viscosity is the reyn. A reyn is 1 lb-sec per sq in. and equals 69,000 poises.

* Strictly speaking, another term, known as the *kinetic energy* or *Couette correction*, should be added. However, this term need be included only in precise measurements. The complete equation is

$$\eta = \frac{\pi r^4 p}{8l} \left(\frac{t}{V} \right) - \frac{1.12\rho}{8\pi l} \left(\frac{V}{t} \right)$$

where ρ is the density of the fluid.

703. Plastic Flow : Bingham Flow. As previously stated, many solids exhibit elastic deformations if the stress is kept within a certain upper limit called the *yield value* or *elastic limit*. However, once this yield value is reached, they undergo flow and permanent deformation. This type of flow is called *plastic flow*. It differs from viscous flow in that it takes place only above a finite yield value. The transition from elastic to plastic behavior may or may not be sharp. More often it is not; *i.e.*, the yield point on the stress-strain curve is not sharply defined.

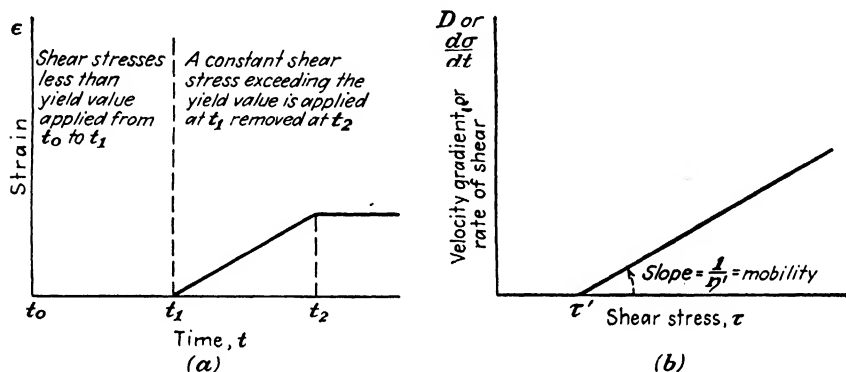


FIG. 7-5. Bingham plastic flow.

The simplest case of plastic flow is that in which the yield point is very sharp and the flow, once started, is linear as in a Newtonian liquid. If rate of shear or velocity gradient D be plotted against shear stress τ , this simplest case is represented by Fig. 7-5b and Eq. (7-8a), which should be compared with Fig. 7-4b and Eq. (7-5).

$$\eta' = \frac{(\tau - \tau')}{D} \quad D = \frac{1}{\eta'} (\tau - \tau') \quad (7-8a)$$

where η' is a constant called the *pseudoviscosity* or *plastic viscosity*, τ the applied shear stress, τ' the yield value (a constant), and $1/\eta'$ the reciprocal of the pseudoviscosity, known as the *mobility*.

Comparing this linear plastic flow with viscous (liquid) flow, the pseudoviscosity η' of the solid is analogous to the viscosity of the liquid, and the analogue of liquid fluidity is called mobility. The strain-time (flow) curve is shown in Fig. 7-5a.

According to Bingham, a plastic solid has a yield value τ' and, if a shear stress τ that exceeds τ' is applied, a constant portion of the stress will be used up in overcoming the "internal friction" of the material and the rest $(\tau - \tau')$ will be taken up in producing plastic flow. Linear plastic flow in accordance with Eq. (7-8a) is often called *Bingham flow*.

As previously stated, the yield point is not always sharp, although the

later stages of flow may still be linear or close to it. The D - τ diagram is then as shown in Fig. 7-6. Three yield values have been defined. τ_l is the *lower yield value*—the stress at which flow is first detectable *under the conditions of test*. τ_u is the *upper yield value*—the stress above which

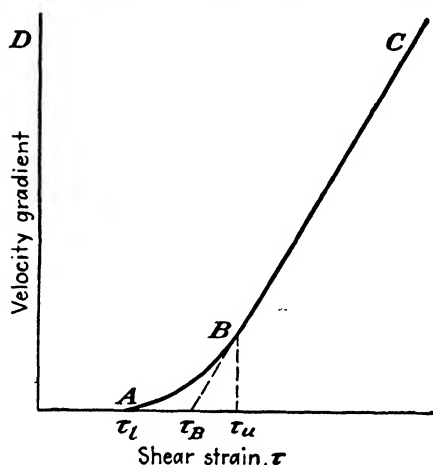


FIG. 7-6. Bingham flow above an unsharp yield value.

the plastic flow becomes linear. τ_B is the *Bingham yield value*—an extrapolated mathematical constant in terms of which the equation for the linear portion of the curve is conveniently written

$$D = \frac{1}{\eta'} (\tau - \tau_B) \quad (7-8b)$$

The flow of a considerable number of plastic materials is satisfactorily expressed by the Bingham equation.

704. Summary. Hookian ideal elastic deformation in a solid and Newtonian flow in a liquid may be considered as two extremes of rheological behavior. It may be said that there are three basic types of deformation, elastic deformation, plastic flow, and viscous flow. The characteristics of the simplest case for each of these three types are summarized in Table 7-2.

TABLE 7-2. SUMMARY OF THE CHARACTERISTICS OF THE SIMPLEST CASE OF THE THREE BASIC TYPES OF DEFORMATION AND FLOW

Type	Simplest case	Character of strain	Relation to yield value	Equation
Elastic deformation	Ideal Hookian	Temporary. Disappears completely and instantaneously on release of stress. Independent of time	Takes place below yield value	$\frac{s}{\epsilon} = E =$ a constant
Plastic flow . . .	Bingham	Permanent. Deformation directly proportional to time	Takes place above yield value	$D = \frac{1}{\eta'} (\tau - \tau_B)$
Viscous flow . . .	Newtonian, or pure, viscous	Permanent. Deformation directly proportional to time	Yield value of material is zero	$D = \frac{1}{\eta} \tau$

A host of materials of industrial importance, including all high-polymer products, exhibit rheological behaviors more complicated than the simple types summarized above. These are shown in Fig. 7-7, which is a classification of rheological properties. They may be considered as modifications and combinations of the three simple behaviors summarized in Table 7-2. Later it will be shown how these complicated cases can be approximated by regarding a material as composed of elastic and viscous elements acting in series, in parallel, or both.

ENGINEERING DEFINITIONS; TESTING OF A STRUCTURAL MATERIAL

705. In order to recall some basic engineering definitions and supply the background for important subsequent considerations we shall digress to consider various aspects of the evaluation of a structural material. A material such as steel or concrete to be used for construction purposes is of necessity a rigid solid. It is given a preliminary evaluation in terms of five basic properties, stiffness, elasticity, resilience, strength, and toughness. The engineering definitions of these mechanical properties and the criteria for their evaluation are presented in Table 7-3.

TABLE 7-3. MECHANICAL PROPERTIES AND THEIR CRITERIA

Property	Practical meaning	Criterion
Stiffness.....	Ability to carry stress without changing dimension	Modulus of elasticity
Elasticity.....	Ability to carry stress without suffering permanent set	Yield point (elastic limit)
Resilience.....	Ability to absorb energy without suffering permanent set	Resilient energy. Area under elastic portion of stress-strain curve
Strength.....	Ability to carry dead load	Ultimate strength, or yield strength
Toughness....	Ability to absorb energy and undergo large permanent set without rupturing	Ultimate energy resistance. Total area under stress-strain curve

These properties are often deduced from stress-strain (load-elongation) curves obtained by loading test pieces of the material in tension, compression, and shear. Figure 7-8 shows the hypothetical tensile stress-strain curve (see note, Fig. 7-10) and will be used to demonstrate how such a curve is employed for evaluating the five basic properties listed in Table 7-3. The Hooke's law region is shown by *OP*. As the applied stress is increased, a point *P* is finally reached beyond which the linear relationship between stress and strain no longer holds. Point *P* marks the *proportional limit*. A point *Y* is found beyond which the deformation

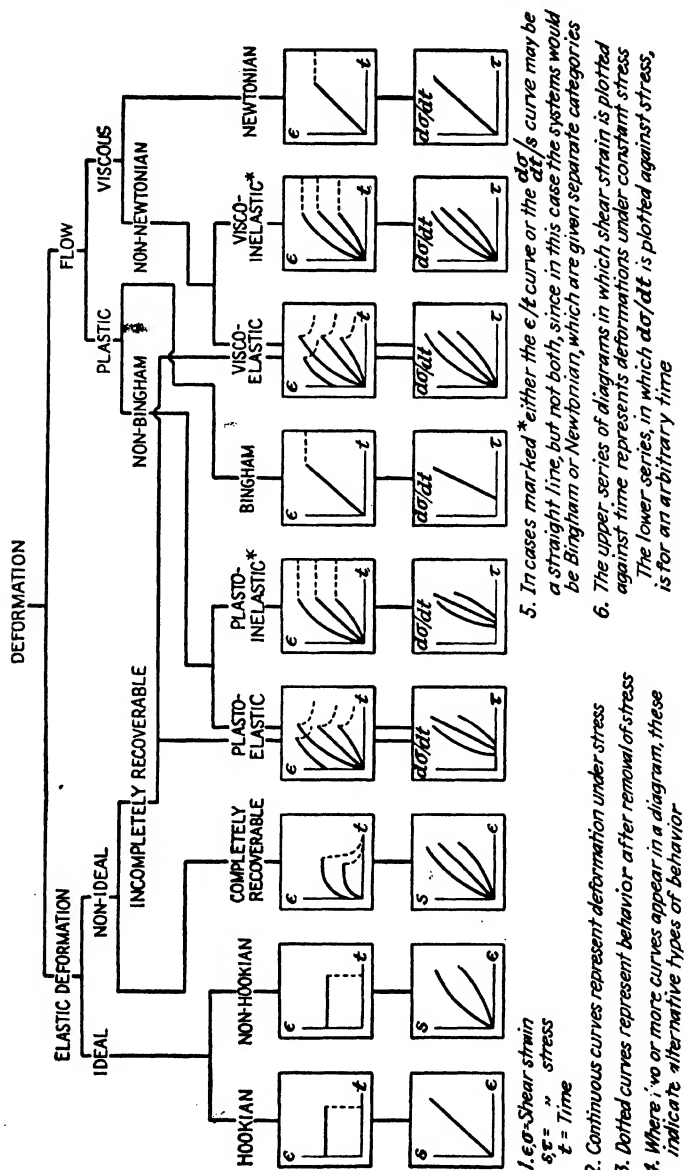


Fig. 7-7. Classification of rheological properties. [British Rheologists' Club, Nature, 149, 702 (1942).]

ceases to be elastic. The point Y is known as the *yield point* or *elastic limit*. For stresses up to s_Y , the material is ideally elastic, *i.e.*, the strain disappears promptly and completely on release of the stress; but it should be noted that up to point P the behavior is Hookean, while between P and Y it is non-Hookean (see also Fig. 7-7). For some materials the yield point is sharply defined and can be detected readily either by a sharp dip

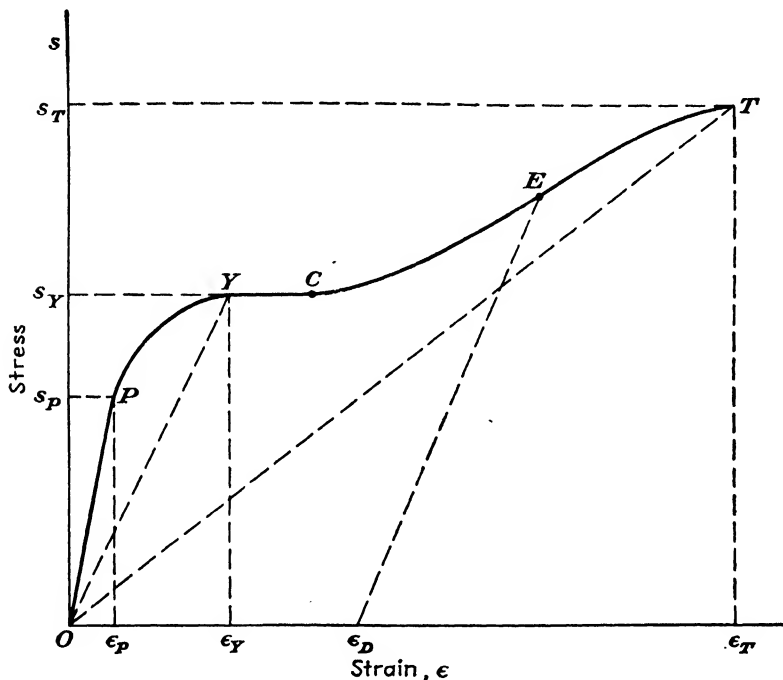


FIG. 7-8. Typical stress-strain diagram with elastic strains exaggerated.

in the curve or by a sudden flattening as shown in Fig. 7-8. In other cases this is not so. At any rate, beyond Y the material is no longer an elastic body but is behaving as a plastic solid. An approximately horizontal section such as YC means that the material is ductile and is flowing under a practically constant stress.

The particular material under consideration undergoes a considerable elongation from Y to C , after which the stress required to effect further elongation again increases (strain hardening) until a maximum called the *ultimate tensile strength* is reached at point T . A second rise in the stress-strain curve as from C to T means that the stress-induced plastic deformations which have taken place between Y and C have resulted in an alteration of structure, which in this case results in *reinforcement*. The material taken out of the testing machine has a different structure than

the sample originally introduced. If the stress is removed after the yield point but before the ultimate strength, *e.g.*, at point *E*, the material will have a permanent set ϵ_D .

The *stiffness* of the material is given by the slope of the elastic portion of the curve and in some cases is reported as the slope of *OP* and in others as the slope of *OY*. The slope of *OP* is, of course, Young's modulus.

The *tangent modulus* at a given stress is the instantaneous slope $ds/d\epsilon$ of the stress-strain curve at that stress. The *secant modulus* between two

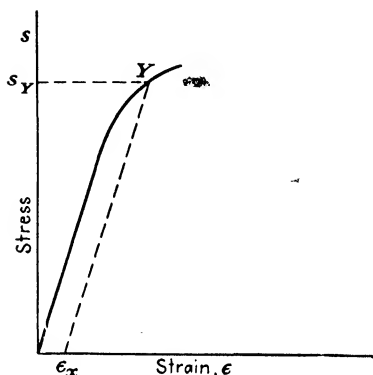


FIG. 7-9. Stress-strain curve of a material without definite yield point.

stresses is the slope of the line joining the two corresponding points on the stress-strain diagram. For example, the slope of *OY* is the secant modulus of elasticity between zero stress and the yield stress; the slope of *OT* is the secant modulus between zero stress and the ultimate tensile stress. When materials exhibit large elongations of a non-Hookian character, notably rubbers and fibers, secant moduli are often of more help in evaluation and comparison than Young's modulus or tangent moduli. The slope of the secant modulus *OT* is sometimes called the *average stiffness*.

Elasticity is measured by the yield stress, or elastic limit, s_Y , which is the stress at the yield point. (For elastomers, the *yield strain* ϵ_Y is of greater significance.)

The *resilience* of the material is evaluated by the area $OPY_{\epsilon_Y}O$ under the elastic portion of the stress-strain curve. This area represents the work required to deform the material to its elastic limit, *i.e.*, the energy that the material can absorb without undergoing permanent deformation. Specifically, the *modulus of resilience*, or *resilient energy*, of a material is the energy required per unit volume to stretch the material to its elastic limit.

Strength is reported in various ways. The *ultimate strength* is s_T , that is, the stress corresponding to the highest point reached on the stress-strain curve. It is obvious that, for materials which are to be used for structural members or parts which must maintain their original dimensions closely, the ultimate strength is not nearly so good a criterion as s_Y , the yield stress. However, a complication is introduced in using the yield stress as a measure of strength in that, as previously mentioned, many materials do not possess a well-defined yield point. In engineering practice this difficulty is overcome by various empirical procedures.

One is to establish an arbitrary *permissible strain* called the *offset* (ϵ_s of Fig. 7-9). A line is then drawn through the offset parallel to the Hooke's law portion of the stress-strain curve, establishing an arbitrary point *Y* on the latter. The stress s_Y , corresponding to this point, is then reported as the *yield strength*.

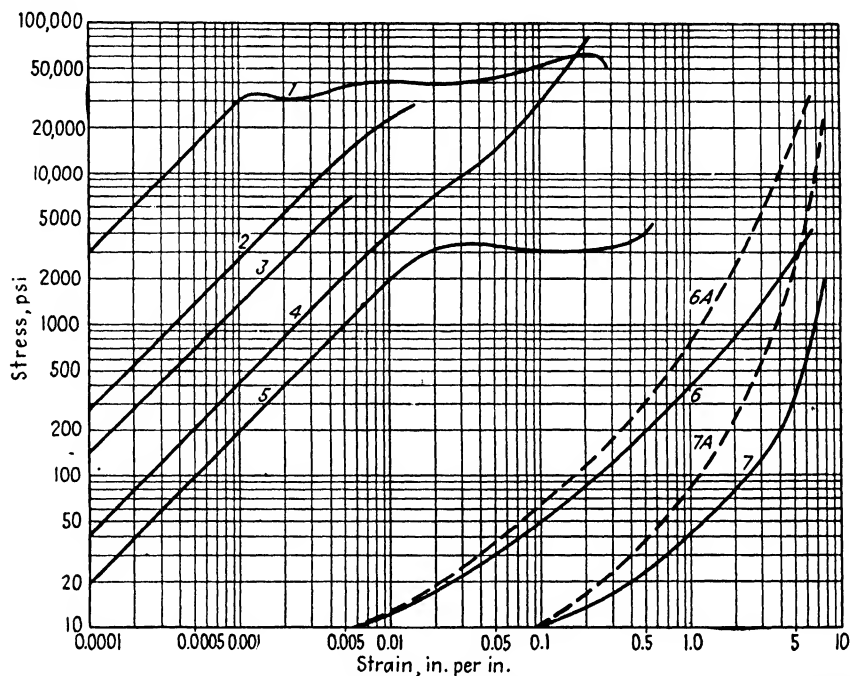


FIG. 7-10. Tensile stress-strain curves for various solids. Curve 1: mild steel. Curve 2: papreg; cross-laminated paper sheets set in phenol-formaldehyde resin. Curve 3: a molded thermoset; wood-flour filler in phenol-formaldehyde resin. Curve 4: nylon fiber, high tenacity. Curve 5: a molded thermoplast; plasticized cellulose acetate. Curve 6: tire-tread rubber; Hevea rubber vulcanizate reinforced with gas black. Curve 7: pure gum vulcanizate; Hevea rubber vulcanizate, no reinforcing filler. Curve 6A: "true" stress-strain curve for material 6. Curve 7A: "true" stress-strain curve for material 7.

In the usual stress-strain curve (such as 1 to 7) the strain is plotted against the stress calculated as the load divided by the original cross-sectional area of the specimen. For a "true" stress-strain curve (such as 6A or 7A), the strain is plotted against the stress calculated as the load divided by the actual cross-sectional area corresponding to that strain. When the strain is small, there is little difference between the two curves, but for a rubbery material that stretches to several times its original length, the difference is enormous.

Toughness is evaluated by the total area $OPYCT_{\epsilon r O}$ under the stress-strain curve. It is the total work that must be done to rupture the material. Specifically, it is the energy required per unit volume of material to cause rupture. It will be noted that resilience and toughness are somewhat allied. This is particularly noticeable if a material has no well-defined yield point. *Brittleness* may be regarded as a lack of

resilience or toughness. The stress-strain curves of various materials in tension differ widely in character, as may be seen from Fig. 7-10.

THE INFLUENCE OF TIME: RELAXATION

706. From the preceding discussion it is evident that the yield value of a material is a characteristic of outstanding practical importance. It is the stress at which deformations cease to be elastic and become permanent, owing to the onset of flow. It therefore marks the limit of usefulness for materials that are to be used for fabricating parts that must stay true to dimension. Indeed, it enters into our primary concepts of the states of matter since rheologically a solid is defined and distinguished from a liquid as a material having a finite yield value. The difference in behavior is a consequence of the "fixed" structure of solids. Because of this structure, flow in solids takes place only by blocks of molecules moving, requiring a finite force. In liquids, however, individual molecules may move so that an infinitesimal force suffices. Nevertheless, the yield value has no fundamental theoretical significance since experimentally it is a function of time and the rate at which stress is applied. As an example, let us assume that the yield value of a particular material is found to be 20,000 psi under the usual (fairly rapid) tensile test to which metal specimens are subjected. If a bar of the material is clamped between jaws and subjected to a tension of 10,000 psi, it will stretch to a certain length. Presumably, if the bar is held at this constant stretched length, the stress should remain at 10,000 psi indefinitely; and when it is released, the bar should return to its original dimensions, having suffered no permanent set. But this is not so. (If held for very long periods of time in the stretched condition, the stress may be found to drop slowly to zero, the bar undergoing permanent set to the stretched length. This phenomenon is known as *relaxation*. What, then, is the yield value of the material? Obviously, determining this is a matter of patience—a matter of how long we are willing to wait before permanent deformation (flow) can be detected by measurement. Such slow, long-time permanent deformation at stresses well below the short-time yield value (as reported from standard testing procedures) are called *creep* or sometimes *cold flow*.

Relaxation and the effect of time may be studied by holding one or the other of the factors of stress or strain constant and determining either or both of two types of curve:

1. *The relaxation curve.* The sample is strained promptly to a given deformation. The strain is then held constant and the (decreasing) stress is measured as a function of time.

2. *The flow curve.* A given stress is applied quickly to the specimen

and maintained constant while the (increasing) strain is measured as a function of time.

If a body is ideally elastic, a tensile strain is accompanied by a stress in accordance with Eq. (7-1) and the rate of strain is

$$\frac{d\epsilon}{dt} = \frac{1}{E} \frac{ds}{dt}$$

The body does not relax, its rheological behavior being analogous to that of a steel spring. On the other hand, if the body possesses viscosity, the flow at constant tensile stress is in accordance with Eq. (7-7) and the rate of flow is

$$\frac{d\epsilon}{dt} = \frac{s}{\eta}$$

If the material possesses both elasticity and viscosity, the state of affairs may be represented schematically as in Fig. 7-11, where it is assumed that the body is composed of an elastic element (spring) and a viscous element (piston and dashpot). In Fig. 7-11a, the pair is placed in series, and this combination is frequently termed a *Maxwell unit*. An example of such a system is a fiber containing a crystalline and an amorphous region (Fig. 2-9). In this case the rate of flow is

$$\frac{d\epsilon}{dt} = \frac{1}{E} \frac{ds}{dt} + \frac{s}{\eta}$$

or

$$\frac{ds}{dt} = E \frac{d\epsilon}{dt} - \frac{E}{\eta} s$$

and

$$\frac{ds}{dt} = E \frac{d\epsilon}{dt} - \frac{s}{\lambda} \quad (7-9)$$

where $\lambda = \eta/E$ is a constant termed the *relaxation time*. The analogous equation for shear stress is

$$\frac{d\tau}{dt} = G \frac{d\sigma}{dt} - \frac{\tau}{\lambda} \quad (7-10)$$

In Fig. 7-11b the pair is placed in parallel. This combination is called a *Voigt unit*. Any deformation takes place equally and simultaneously in the spring and piston. Mechanically, this system behaves like a retarded steel spring.

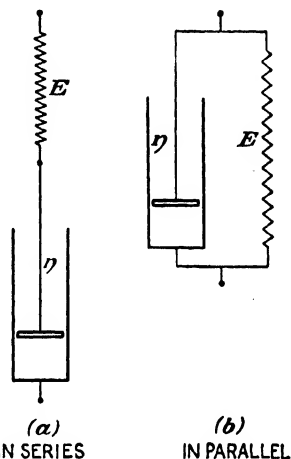


Fig. 7-11. Mechanical model of relaxation using an elastic and a viscous element. (a) In series (b) In parallel.

707. Relaxation under Constant Strain (Relaxation Curve). If a body made up of an elastic and a viscous element in series as in Fig. 7-11a is given a certain strain that is held constant, the deformation will originally occur entirely in the spring; but as time passes, flow takes place in the viscous element (the piston moves) and the stress is progressively dissipated.

Since in this case ϵ is held constant, $d\epsilon/dt$ is zero and the residual stress after a time t may be found by integrating Eq. (7-9), giving

$$s = s_0 e^{-t/\lambda} \quad (7-11)$$

where s_0 is the original stress. This is the equation for the so-called "relaxation curve," and the relaxation time λ is the time necessary for the stress to decrease to $1/e$ of its original value.

If a body made up of an elastic and a viscous element acting in parallel as in Fig. 7-11b is given a stress with the aim of achieving a particular strain, the stress required will depend upon the rate of deformation. In any case, once the desired strain is achieved, the stress is constant at the value s . It is evident that this system does not provide any relaxation mechanism under constant strain.

708. Relaxation under Constant Stress (Flow Curve). Consider the above combinations at constant stress. For the elastic and viscous elements in series (Fig. 7-11a), on integrating Eq. (7-9)

$$\epsilon = \frac{s}{E} + \frac{s}{\eta} t = \frac{s}{E} + \frac{s}{E} \frac{t}{\lambda} \quad (7-12)$$

which is the equation for the so-called *flow curve* (Fig. 7-12a). This is also written more generally

$$\epsilon = \epsilon_0 + v_0 t \quad (7-13)$$

where v_0 is the *creep rate*.

For the elastic and viscous elements in parallel (Fig. 7-11b), the piston starts moving at a rate s/η , which decreases asymptotically to zero as the stress is gradually transferred to the spring (Fig. 7-12b). A reinforcement therefore takes place during flow. The rate of flow at any instant is given entirely by the rate of flow of the viscous element, but the stress on the viscous element is the external stress decreased by the stress in the elastic element.

$$\frac{d\epsilon_R}{dt} = \frac{s - \epsilon_R E}{\eta} \quad (7-14)$$

This yields, on integration,

$$\epsilon_R = \frac{s}{E} (1 - e^{-(E/\eta)t}) = \epsilon_\infty (1 - e^{-t/\lambda}) \quad (7-15)$$

where $\epsilon_{\infty} = s/E$ is the elongation at infinite time. This is the equation for the flow curve (Fig. 7-12b). We have here a *retarded elastic deformation*. Retarded elastic strains are involved in most deformations of high polymers, especially in the phenomena generally called *creep recovery*, *elastic after-effect*, or *elastic memory*.

709. Relaxation Effects. Plastics, rubbers, fibers, and many metals behave as though they contained both elastic and viscous elements.

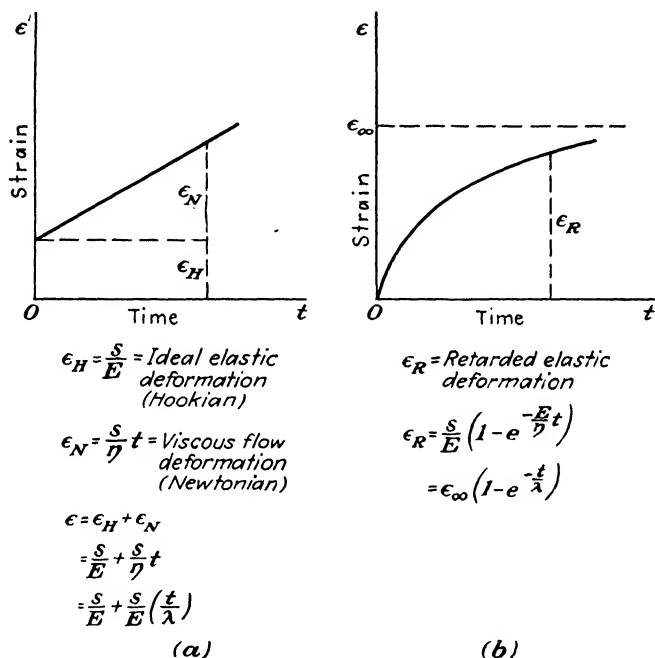


FIG. 7-12. Constant-stress flow curves of an elastic and a viscous element. (a) In series. (b) In parallel.

There is a measurable relaxation time, and such phenomena as cold flow, creep, and fatigue are common and of great practical importance. The yield value is a function of time and rate of loading. It follows that, if such materials are to be compared from stress-strain curves, the conditions of test must be carefully standardized with respect to rates of loading and deformation and the yield value must be defined empirically as the stress at which flow first becomes observable under precisely stipulated conditions of test.

In general, the relaxation effect is the more noticeable the less crystalline and homogeneous the material and the lower the forces of attraction between its structural elements. For an ideally elastic body, the relaxa-

tion time is infinite. For a Newtonian liquid, it is vanishingly small. The following examples of the time effect will suffice at this stage:

1. A piece of pitch struck a sharp blow shatters with very little extension. In other words, when stressed rapidly under impact, it behaves like a brittle solid. The same pitch stressed slowly flows as a highly viscous liquid.

2. A sample of raw rubber was found to behave as shown in Table 7-4.

TABLE 7-4. EFFECT OF RATE OF EXTENSION ON TENSILE BEHAVIOR OF RAW RUBBER AT 20 C

Rate of extension %/sec	Time to break	Tensile strength, psi	Elongation at break, %	Secant modulus of elasticity at 100% elongation, psi
50	20 sec	450	1,250	76
3	5 min	145	1,020	57
0.025	4 hr	31	300	31

ROSBAUD, V. P., and E. SCHMID, *Z. tech. Physik*, **9**, 98 (1928).

3. The ultimate tensile strength and, in fact, the entire stress-strain curve of a fiber are raised when the stress is applied at a rapid rather than a normal rate. The magnitude

of the effect is shown in Fig. 9-6.

4. The ultimate tensile strength of brittle solids is decreased with time of duration of the stress [Eq. (7-28), page 309].

It will be noticed that Eqs. (7-11), (7-12), and (7-15) contain the ratio t/λ , which is the ratio of the action time to the relaxation time for the material. The smaller this ratio, the less the relaxation and the more elastic the behavior. Conversely, the larger this ratio, the more viscous the behavior.

710. Hysteresis. A certain amount of the work done in deforming a solid is dissipated as heat. This is measured by de-

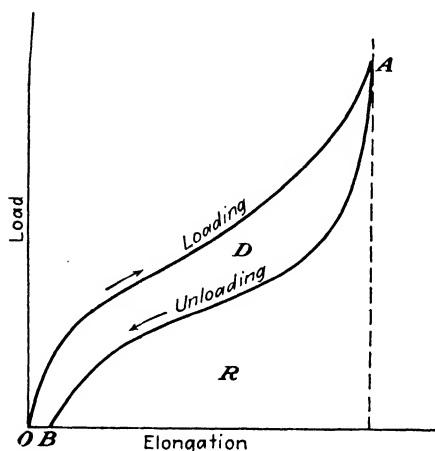


FIG. 7-13. Elastic hysteresis. Area under curve OA is total work of extension and equals $D + R$. Area under curve AB is work of retraction and equals R . Work converted into heat equals area of hysteresis loop equals D . Specific damping capacity equals $D/(D + R)$.

termining the stress-strain curve through a cycle of loading and unloading. It is found that the path followed during extension is not the same as that for retraction. This is illustrated in Fig. 7-13. The total work

of extension is given by the area under the loading curve OA . The work of retraction is the area under AB , and the area D of the enclosed hysteresis loop represents energy dissipated as heat. The phenomenon is known as *elastic hysteresis* and is observed with all solids, including metals, fibers, plastics, and rubbers. For an ideally elastic Hookian body, the paths followed during loading and unloading coincide, and there is no loop. For imperfectly elastic bodies, on the other hand, especially those which undergo changes in structure during extension, there is a loop. The loop is therefore very different in size and shape for different materials. For steels it is very small. That shown in Fig. 7-13 is typical of vulcanized rubber. The size of the loop is very important in indicating how much a material will heat up when subjected to cyclic stresses and also how well it will dampen vibrations.

MOLECULAR THEORY AND RHEOLOGICAL BEHAVIOR

The extent to which current physicochemical theories of the structure of matter account for its rheological and mechanical properties will now be discussed.

711. Crystalline Solids. Let us consider a crystal consisting, for the sake of discussion, of but one kind of atom and held together by strong primary valence forces. The potential energy between two halves of the crystal along a given crystal plane is shown by a typical potential-energy curve (Fig. 7-14a). By differentiating this potential-energy function we get the curve of Fig. 7-14b, which represents the force between the crystal halves as a function of the distance between them, r' . This force reaches a maximum at the distance r'' . This maximum represents the force theoretically necessary to pull the crystal apart and is thus the theoretical tensile strength. r_0 is the distance of normal approach, *i.e.*, the distance between the mean equilibrium positions of two neighboring atoms when the crystal is not acted upon by external stress. At this distance, the force between the atoms is zero, the potential energy is at a minimum, and each atom is at the bottom of a potential energy trough e_m . In the crystal under consideration, this trough is very deep since we have postulated strong primary valence forces. Owing to the regularity of position and arrangement, the potential troughs for the atoms along

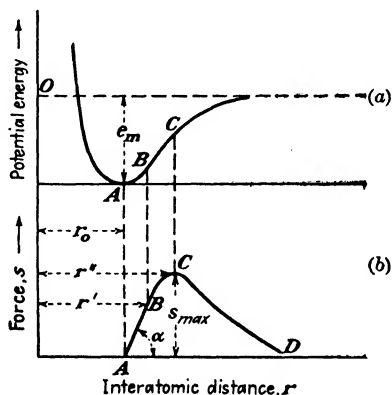


FIG. 7-14. Mechanical properties of an ideal crystal in terms of the potential energy function.

the crystal plane are of regular depth and are congruent, as shown schematically in Fig. 7-15a.

Each atom vibrates rapidly about its mean center owing to thermal agitation; but the mean amplitude of this vibration is only a few per cent of r_0 , and, owing to the steepness of the trough, the escape of an atom from one equilibrium position to another due to thermal motions is extremely infrequent. In other words, to all intents, self-diffusion is nonexistent, and no internal flow or change of dimension occurs in the unstressed mass.

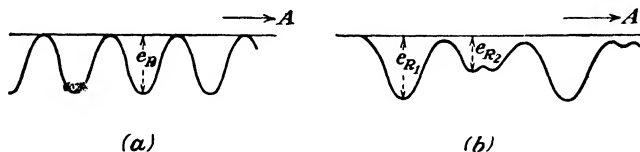


FIG. 7-15. Schematic representation of potential troughs. (a) Along a lattice plane in a crystalline body. (b) Along a random section of an amorphous body. (R. Hovink, "Plasticity, Elasticity and the Structure of Matter," 1940. By permission of The Macmillan Company, publishers, and Cambridge University Press.)

If sufficient stress is now applied (assume tension) to pull the two crystal halves apart to a distance r' , potential energy is absorbed by the atoms. However, this absorbed energy is not sufficient to carry the atoms "over the hump," and they do not leave their troughs. When the external stress is released, they return instantaneously to their original equilibrium positions (ideally elastic deformation). In the case under consideration, the portion of the force curve between A and B (Fig. 7-14b) is almost a straight line and has, moreover, a steep slope. As a consequence, the material has a high elastic modulus and the deformation postulated above, besides being ideally elastic, is also Hookian.

Progressive increase of the externally applied tension pulls the atoms apart against a continually increased resistance until the interatomic distance r'' is reached at point C . Thereafter it drops again. The force s_{\max} is therefore the theoretical tensile strength and should also be the yield stress since theoretically the material is perfectly elastic all the way to the point of rupture C . Furthermore, the crystal should yield sharply since each atom is in a potential trough of identical depth. Theoretically, the elongation at break is $\Delta r = r'' - r_0$ and is small since the slope of AC is steep. For the same reason, the crystal should lack toughness.

To summarize, current molecular theory predicts that a primary-valence crystal should have the following properties: It should exhibit small, ideally elastic Hookian deformations, the strains representing temporary distortions of normal bond angles or bond lengths. These temporary displacements of the structural elements from their well-defined equilibrium positions can take place without interchange of

position. The strains disappear at once upon release of the external stress. The yield point may be sharply defined. In terms of Table 7-3 the crystal may exhibit the following combination of properties: stiffness, rigidity, strength, hardness, brittleness, and nonductility. Many ionic and metallic crystals, quartz, and the diamond do, indeed, fall into this category.

How might a primary-valence crystal be able to undergo permanent plastic deformations rather than elastic ones? Since a crystal is of necessity anisotropic, the resistance to stress is greater along some crystal planes than others. Under stress, whole layers of atoms or molecules may slip along *glide planes* of least resistance. Figure 7-16 is a schematic representation of a plastic deformation due to slip along a crystallographic plane. The phenomenon is commonly observed in metals, where it is extremely important, and has also been encountered in ionic crystals, ice, etc.

A discussion of the effect of temperature is particularly informative at this point. In the primary-valence crystal previously discussed, each atom vibrates in an energy trough. The depth of this trough may be designated by e_R (Fig. 7-15a). Owing to thermal agitation the atom vibrates in all directions with a frequency of about 10^{13} per second. It is unable to escape from the trough (flow) only so long as e_R exceeds the energy impulse corresponding to the largest thermally induced vibration. From kinetic theory, the *mean* interatomic energy is $3kT$ (where k is the Boltzmann constant), and at every temperature there is a *mean* amplitude of vibration. But there is also a distribution of vibration amplitudes. This means that at *any* temperature the value of e_R will on occasion be momentarily exceeded, permitting an atom to escape from its trough. Such a migration would constitute flow at zero stress. Hence, the yield value of all materials is *theoretically* zero. The extent of this self-diffusion or flow is a function of time; for, the longer one waits, the greater will be the chance that atoms will vibrate with sufficient amplitude to escape

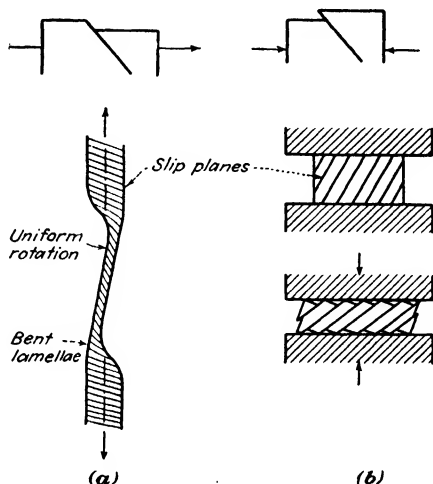


FIG. 7-16. Permanent deformation in a primary-valence crystal by slippage along a crystallographic plane owing to (a) tensile stresses, (b) compressive stresses. (C. S. Barrett, "Structure of Metals," McGraw-Hill Book Company, Inc., New York, 1943.)

from their troughs. Furthermore, an externally applied directional stress will increase the number of migrations per unit time and give them direction. The frequency of these thermally induced migrations can be calculated from theory. In metallic silver at room temperature the mean time required for the migration of an atom from one trough to another is of the order of 100,000,000 years. In this case, therefore, the effect of self-diffusion is so small as to be unmeasurable; and, at all real rates of testing, silver at room temperature has a finite yield value. The relaxation time, practically speaking, is infinite. Equation (7-28), page 309, correlates several of these quantities for brittle materials.

If the temperature is raised to the melting point, the *mean* amplitude of vibration is such that all the atoms of the crystal can escape from their energy troughs many times a second. Under these conditions the crystal lattice collapses, the yield value is zero, and the material is a liquid. The relaxation time is practically zero.

Crystalline solids often have sharply defined yield points. Amorphous solids do not. In a crystal, owing to the regularity of arrangement of the crystal elements, the potential troughs along a lattice plane are of regular depth and congruent, as shown schematically in Fig. 7-15a. The energy required to remove each atom or molecule from its trough is the same, and the yielding under stress will therefore tend to be sharp.

If, in similar fashion, we represent the potentials along a random section of an amorphous body, the troughs are of differing depths (Fig. 7-15b). In certain amorphous materials some troughs may even be encountered where e_R is zero. At any rate, the tension necessary to draw different atoms or molecules out of their troughs will vary considerably. Every increment in external stress will enable a new fraction of the molecules to migrate (flow). Consequently, the yield value of the amorphous body cannot be sharp. The flow-stress curve will be curvilinear as in *AB* of Fig. 7-6. A stress might finally be attained above which further increases in stress would no longer increase the number of "flowing molecules." In that event we should have an upper yield value (τ_u of Fig. 7-6). It could be assumed that every increase in stress above this upper yield value might be utilized, not for "loosening up" additional molecules, but rather for increasing the rate of slip of one plane of molecules past another, *i.e.*, increasing the rate of laminar flow. If such were indeed the case, the flow-stress curve would become linear above the upper yield point (*BC* of Fig. 7-6). Straight-line flow such as *BC* is variously called *linear* or *pure* flow. Curvilinear flow such as *AB* is known as *anomalous* or *quasi* flow. We have here a theoretical explanation for lower and upper yield points and linear and anomalous flow.

From now on, we may consider a yield value as a kink or point in a

flow-shear or stress-strain diagram, having little theoretical meaning, but of considerable practical significance if a material is being tested by a carefully standardized method.

712. Quantitative Aspects. How far does current theory enable the quantitative estimation of mechanical properties? The potential-energy functions of simple metallic, ionic, and even some simple molecular

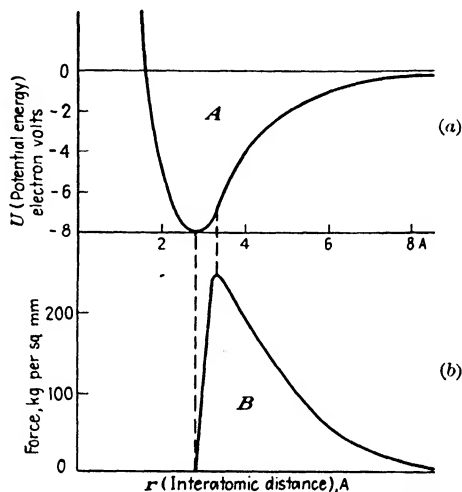


FIG. 7-17. Potential energy and force between two halves of a NaCl crystal separated by a (100) plane. (H. Mark, in "Cellulose and Cellulose Derivatives," E. Ott, editor, Interscience Publishers, Inc., New York, 1943).

crystals are known with considerable accuracy. For example, the potential energy between two halves of a sodium chloride crystal on a 100 plane is as shown in Fig. 7-17a. The previous discussion implies that many mechanical properties should be calculable from this curve. The area under the force curve is the total energy required to separate

TABLE 7-5. COHESIVE-ENERGY VALUES FOR DIFFERENT TYPES OF SINGLE CRYSTALS

Substance	Cohesive energy, kcal/g mole	
	Observed	Calculated
Li	39.0	36.1
Na	26.0	23.5
Be	53 to 36	75
NaCl	183	183
LiH	281.5	218
CO ₂	8.24	7

the ions by dissociation, the so-called *cohesive energy*. It has been determined experimentally with a high degree of accuracy for several substances from thermochemical and electrical measurements. The experimental and calculated values are in good agreement for some simple crystalline materials, as shown in Table 7-5.

The elastic constants of a material are also related to the potential-energy function. One of the simplest cases to study is uniform compression of a homogeneous material in all directions. The compressibility coefficient κ has been calculated from the potential-energy function, and the values agree satisfactorily with experiment. Table 7-6 contains a few cases where the agreement is particularly good.

TABLE 7-6. COMPRESSIBILITY VALUES FOR SINGLE CRYSTALS

Substance	Reciprocal compressibility ($1/\kappa$) (10^{11} dynes/sq cm)	
	Observed	Calculated
Na	0.85	0.88
Cu	13.9	14.1
NaCl	41.6	43.5

SEITZ, F., "The Modern Theory of Solids," McGraw-Hill Book Company, Inc., New York, 1940.

This close agreement is encouraging confirmation of the underlying soundness of current theory. Unfortunately, however, when attempts are made to calculate such all-important technical properties as tensile strength and elongation at break, very little success is encountered even for simple crystals, let alone complicated materials like polycrystalline metals and imperfectly crystalline fibers, plastics, and rubbers.

In the present state of our knowledge, a potential-energy function such as is shown in Fig. 7-17 can be calculated only for a perfect crystal. Disturbances due to flaws and mechanical imperfections cannot be coped with since the number and distribution of the flaws in a real sample are not known although they are unquestionably present. For example, in the case of sodium chloride, the tensile strength from Fig. 7-17 is 3.5×10^6 psi. The experimentally observed value is only 0.2 per cent of this.

One explanation for this enormous discrepancy is that a real crystal has weak spots in the form of points of high localized internal stress. These may be internal flaws due to imperfect crystallization or, still more important, notches on the surface of the specimen in the form of scratches or tiny surface cracks. The surface forces (Sec. 216) acting at a solid surface may not be the same in all directions owing to nonuniformity,

crystallization, or preferred molecular alignment. Such disparity of forces may result in the formation of minute surface cracks or flaws at which rupture under stress readily begins. Another interpretation of the inception of fracture at the surface of brittle solids does not require the postulation of previously existing surface scratches. The failure of the bonds between two successive layers of the structural elements of a crystal under stress takes place when the bonds have been excited to the required energy level [Eq. (7-28)]. Molecules at the surface have a higher energy content than those in the interior so that they are partly activated and consequently bonds fail more readily at the surface.

Rupture, once started at a notch, continues progressively *across* the specimen. Instead of being *pulled* apart axially, the crystal halves are progressively *stripped* apart, beginning at the flaw. Spectacular evidence supports this idea. By keeping sodium chloride crystals under hot water and thereby presumably dissolving away the surface cracks or scratches, experimental tensile strengths up to 85 per cent of theoretical have been obtained, instead of the 0.2 per cent by ordinary procedure. The above is a manifestation of what is generally called the *notch effect*.

A more familiar illustration of the notch effect is the following. An undamaged sheet of cellophane is difficult to tear; but if a notch is cut in the edge, it parts readily, the path of failure beginning at the notch and traveling progressively across the sheet. Evidently a high localized stress is introduced at the notch, which results in a loss of factual, though not intrinsic, strength. Similar losses of resistance to external stress are observed in the introduction of holes, bends, or abrupt changes of section in any test specimen.

From theoretical considerations, the more capable of relaxation a material is, the less notch-sensitive it should be since the relief of localized stress, whether on the surface or in the interior, should prevent the formation and propagation of cracks or flaws. Brittleness and stiffness should be associated with high, toughness and plasticity with low, notch sensitivity. This is indeed the case. In line with previous discussion, polished specimens often have higher strength values than ordinary ones, presumably because cracks and scratches (fine notches) have been eliminated from the surface. But the matter may go much further. X-ray diffraction studies show that in crystalline solids, especially metals, fine polishing removes high points and deposits the substance from them in the crevasses, giving rise to a film of transparent disorganized amorphous material called the *Beilby layer*. This layer is decidedly more plastic than the interior, and its presence presumably minimizes surface flawing.

When it comes to calculating the strengths of high polymers, the situation is enormously more complicated than it is for simple perfect crystals. There are crystalline and amorphous elements simultaneously present in various degrees of orientation, the molecules are of different lengths, and owing to their unusual size there are long-range effects not present in simpler substances (Sec. 951).

713. Summary. To summarize, elasticity, stiffness, and high yield values are encountered in primary-valence crystals. Steep potential troughs result in high yield values. Perfect crystallinity tends to result in *sharp* yield values. Secondary-valence crystals (shallower potential troughs) have lower values. Still lower yield values are encountered in systems where the structural units are particles of colloidal size and the resistance to external stress is due merely to surface forces. Table 7-7 is informative.

TABLE 7-7. ELASTIC PROPERTIES OF SOLIDS

Mechanisms involved in elastic deformation	Typical examples	Elastic modulus		Range of elastic extensibility, %	Dependence upon temperature
		Dynes/sq cm	Psi		
Stretching of primary valence bonds.	Ionic bonds: salts. Metallic bonds: nickel. Covalent bonds: diamond	5×10^{12} to 5×10^{11}	7×10^7 to 7×10^6	0.1-0.5	Slight. Proportional to $1/T$
Bending of covalent primary bonds.	Quartz, diamond	5×10^{11} to 5×10^{10}	7×10^6 to 7×10^5	0.2-0.8	Slight. Proportional to $1/T$
Stretching of hydrogen bonds.	Ice	5×10^{11} to 5×10^{10}	7×10^6 to 7×10^5	0.2-0.8	Slight. Proportional to $1/T$
Stretching of van der Waals' bonds.	Sucrose, phthalic anhydride, naphthalene	10^{11} - 10^{10}	14×10^5 to 14×10^4	0.5-1.5	Slight. Proportional to $1/T$
Stretching of secondary valence bonds combined with kinetic elasticity (uncoiling) of high-polymer chains.	Strong forces: cellulose, nylon, proteins	10^9 - 10^8	15,000 to 1,500	Up to 1,000	Proportional to T
	Medium forces: polyesters, polyvinyl alcohol	10^8 - 10^7	1,500-150		
	Weak forces: hydrocarbon polymers	10^7 - 10^6	150-15		

Heterogeneity and low degree of crystallinity tend toward unsharp yield values. Owing to thermal agitation all bodies tend to relax even under zero stress. Hence, theoretically, the yield value of all materials is zero. Practically this is not the case, but it is a fact that yield values, elongations, and "strengths" depend upon the rate of testing. Conditions of test must therefore be carefully standardized if the mechanical and rheological properties of different materials are to be informatively compared and evaluated. Although good agreement between calculated and observed values of cohesive energies and elastic constants for some simple crystals constitutes heartening confirmation of our physicochemical theories, such practically important properties as strength and elongation at break cannot be quantitatively calculated. The effect of flaws is overshadowing. Conditions are greatly complicated in high-polymeric masses. They contain both crystallites (elastic elements) and amorphous regions (viscous elements); and, as will be elaborated later, there are effects of long-range entanglement that do not exist in low-molecular-weight structures.

714. Low-molecular-weight Liquids. Consider a liquid composed of small molecules. The best available evidence is that the nearest neighbors of any individual molecule are arranged about it in somewhat orderly fashion, much as in the crystalline state, but molecules a few angstroms removed are in practically random relationship. Owing to thermal agitation and the existence of holes in the structure, the molecules exhibit continuous Brownian movement. When one approaches another, it is held momentarily by an intermolecular attraction. It remains for a very short time, changes its direction, and leaves again. These motions are random with regard to direction. As in a solid, each single particle vibrates around a mean center, but this center is not fixed. In other words, in a liquid there are small "cybotactic groups" arranged in orderly fashion, but there is no rigid, long-range ordered structure such as exists in a solid.

This internal fluidity prevents the liquid from sustaining static tensile or shearing stresses and from maintaining a definite shape. If even an infinitesimal stress is applied, internal flow and relaxation are practically instantaneous. The yield value is therefore zero. The mass is incapable of elastic deformation. Potential energy cannot be stored during deformation. The work performed during deformation is completely lost from a mechanical point of view. It is all converted into heat.

Viscosity has been described as an internal resistance of the liquid to an externally applied force inducing flow. How, if the yield value is zero, can the viscosity have a finite value? The viscosity is a resistance against the slippage of one *plane* of molecules past a neighboring plane.

To cause such a steady, continuous *unidirectional* motion of an entire plane of molecules past another, a continuous driving force must be exerted to overcome the intermolecular attractions acting between the two liquid planes. Hence the viscosity has a finite value. Without a *sustained* shearing force, unidirectional (laminar) flow ceases although the randomly directed Brownian motions of self-diffusion that result in the zero yield value continue. Our picture of a simple liquid is thus one of a mass devoid of elasticity and possessing only viscosity, in contrast with an ideally elastic solid, which possesses only elasticity and is devoid of viscosity.

In these theoretical terms, evidently in a simple liquid an applied stress is used entirely to produce internal shearing of the liquid, the rate of shear or flow is directly proportional to the applied shearing stress in accordance with Newton's equation, and the amount of flow is a linear function of time. All low-molecular-weight liquids such as water, mercury, and benzene exhibit this pure viscous flow [Eq. (7-5), page 261].

TABLE 7-8. FLOW PROPERTIES OF VARIOUS CLASSES OF LIQUID

Moving element	Average volume, A ³	Average energy of activation, kcal per moving element	Viscosity at melting point, poises	"Relaxation time," sec	Typical example
Single atoms	10	1	10 ⁻³	10 ⁻¹³	Argon
Single molecules:					
Weak forces	50-500	2	10 ⁻²	10 ⁻¹²	Pentane
Medium forces . . .		3-4	10 ⁻¹⁻¹	10 ^{-11-10⁻¹⁰}	Acetaldehyde
Strong forces . . .		4-6	1-10	10 ^{-10-10⁻⁹}	Octyl alcohol
Aggregates of molecules	10 ^{2-10⁴}	10	10-10 ²	10 ^{-9-10⁻⁸}	Glycerol
Segments of macromolecules . .	10 ^{2-10⁴}	20-40	10 ^{3-10⁵}	10 ^{-7-10⁻⁵}	Vinyl polymers
Aggregates of macromolecules . .	10 ^{6-10⁸}	>100	>10 ⁵	>10 ⁻⁵	Cellulose esters

MARK H., in "Cellulose and Cellulose Derivatives," E. OTT, editor, Interscience, Publishers, Inc., New York, 1943.

In accordance with the above picture, the magnitude of the viscosity will depend upon the intermolecular forces of attraction and all factors that determine the latter, *viz.*, molecular size, shape, polarity, etc., and temperature should exert an influence. That this is indeed the case should be confirmed by comparing the viscosities of various liquids. Strongly polar liquids have higher viscosities than nonpolar liquids. Spherical molecules contact one another at essentially one point, whereas rod-shaped molecules have a greater surface of contact. Hence normal heptane has a higher viscosity than the isoheptanes, and in a homologous

series the higher members have the greater viscosities. As a result, viscosity measurements may be used as a basis for molecular-weight determinations. When molecules are very long, the effect of long-range entanglement manifests itself, introducing a complicating factor in the viscosity functions. A general correlation of the type of flowing element, intermolecular forces, and flow characteristics of the liquid is presented in Table 7-8.

The viscosity of a liquid is strongly dependent on temperature, decreasing rapidly as the temperature increases. For low-molecular-weight organic liquids, the relation is approximately that shown in Fig. 7-18.

For a Newtonian liquid, the temperature dependence of viscosity is reflected in a change of slope of the D - τ line as shown in curves 1, 2, and 3 of Fig. 7-19. If the liquid crystallizes sharply to a solid that happens to exhibit Bingham flow, the state of affairs below the melting point is shown by curves 4 and 5.

715. Solutions and Suspensions. Dissolved and suspended particles in a liquid interfere with the motion of the solvent molecules and cause an increase in viscosity. Various equations giving the effects of concentration and shape of suspended particles and of molecular weight of

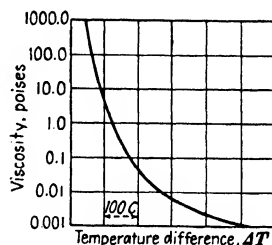


Fig. 7-18. Viscosity-temperature relation for liquids. (T. B. Drew and R. P. Genereaux, in "Chemical Engineers' Handbook," J. H. Perry, editor, McGraw-Hill Book Company, Inc., New York, 1941.)

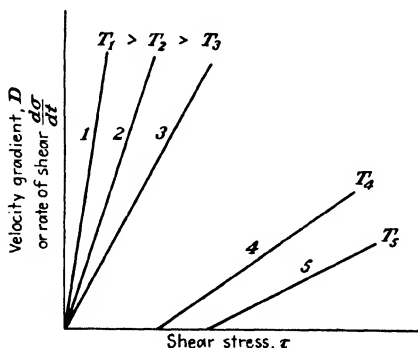


Fig. 7-19. Effect of temperature on viscosity, plasticity, and flow behavior. Temperatures decrease in order T_1 to T_5 . T_1 , T_2 , and T_3 are above melting point, while T_4 and T_5 are below melting point.

dissolved high-polymer molecules have been presented in Secs. 624 and 625. These equations assume the flow to be Newtonian. Actually, as Fig. 7-20 indicates, the flow of the concentrated systems is usually non-Newtonian, so that the constants and perhaps the mathematical form of the equations [e.g., Eqs. (6-41) and (6-46) to (6-48)] will differ for

different velocity gradients. If desired, the measured viscosities may be corrected to a particular rate of shear. However, as Fig. 7-20 indicates, for the more dilute solutions, in which the specific viscosity is less than 0.5, there is probably not much change in viscosity produced by the variations in shearing stress usually met with in the measuring instru-

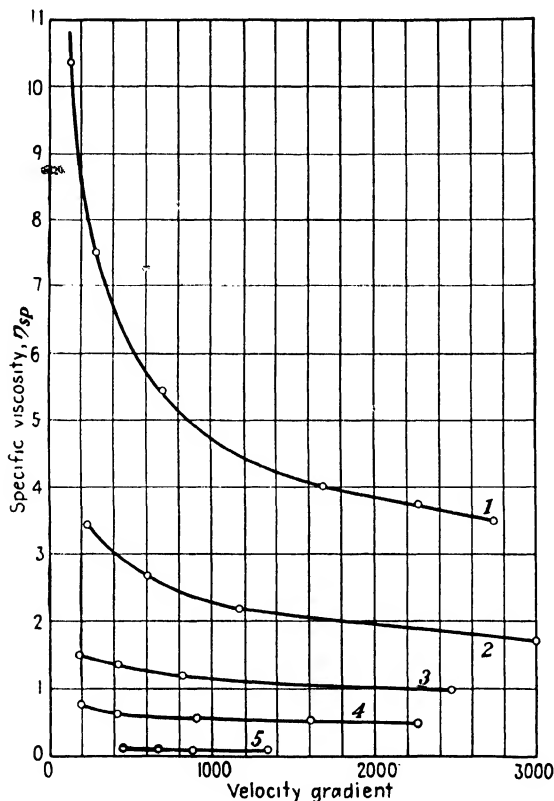


FIG. 7-20. Effects of velocity gradient and concentration on viscosity of high-molecular-weight polystyrene in tetralin. Curve 1: 0.40%. Curve 2: 0.20%. Curve 3: 0.10%. Curve 4: 0.05%. Curve 5: 0.01%. (R. H. Ewart, in "Advances in Colloid Science," Vol. 2, Mark and Whittby, editors, Interscience Publishers, Inc., New York, 1946.)

ments. Therefore, correction to a particular rate of shear is not necessary in molecular-weight measurements, for the intrinsic viscosity [Eq. (6-44), page 248], the quantity needed for calculating molecular weight, is obtained by extrapolation to infinite dilution, at which the flow is, always Newtonian.

716. Anomalous Flow. There are many liquids, concentrated suspensions, emulsions, and gel-like solids for which, unlike Newtonian liquids, the D - τ curve is not a straight line (Figs. 7-23 and 7-24). In systems

showing this *anomalous*, or *quasi, flow*, the rate of shear or flow is a function not only of the shear stress but also of time and the previous history of the sample. Many colloidal and high-polymer dispersions fall into this category. It has now become clear that anomalous flow occurs when, for any reason, some of the applied stress is used for any purpose other than the normal shearing of the mass. It is not proper to speak of the viscosity of non-Newtonian liquids. Instead, we must apply such terms as apparent viscosity, "viscosity," or consistency.

Anomalous-flow phenomena are found to fall into three general categories:

1. Irreversible isothermal changes in consistency resulting from shear
2. Isothermal reversible *increases* in consistency with increasing rate of shear
3. Isothermal reversible *decreases* in consistency with increasing rate of shear

717. Irreversible Changes in Consistency Due to Shear. Many protein solutions, when subjected to high rates of stirring (shear), suffer permanent decreases in viscosity. The same effect has been observed in solutions of many synthetic high polymers. These losses in viscosity appear to be the result of mechanical degradation of the large molecules, much as raw rubber loses consistency when it is worked (masticated) between differential rollers (Sec. 1303). Milk, on the other hand, shows a permanent increase in consistency after subjection to high shear rates, the process called *homogenization*. One explanation is that the fat globules are broken down to much smaller sizes by the shearing action and that their surface area is thus increased. Milk proteins (emulsifying agents) are adsorbed in the surface, and the total forces acting between the fat globules and aqueous serum are increased, resulting in an increased resistance to flow.

The work hardening of metals is an irreversible increase in consistency induced by shear. So is the increase in strength effected by the cold-drawing of nylon and other fibers.

It appears to be common to these phenomena that the shearing action and accompanying flow result in an alteration of structure.

718. Reversible Isothermal Increase in Consistency with Increased Rate of Shear. Wet sand appears to dry when it is stepped on and then become wet again when the foot is raised. Similar behavior has been observed in concentrated suspensions of certain fine powders such as rice starch granules and powdered quartz in appropriate liquids. Thus, if quartz powder (1 to 5 μ) carefully freed of electrolytes is mixed with water so that the volume fraction of the quartz is 43 to 45 per cent, the mass appears wet and, when stirred slowly with a spatula, behaves like a viscous

Newtonian liquid. At faster rates, the resistance to stirring rises to a spectacularly disproportionate value, and the appearance changes to that of a rather dry mass. Immediately after stirring is halted, the system appears wet again and once more flows like a viscous liquid. The mass will exhibit this change in apparent viscosity any desired number of times. Freundlich called this phenomenon *dilatancy*. In this text the term will be used to describe any isothermal reversible *increase* in consistency or apparent viscosity with increased rate of shear. The term *inverse*, or *negative, thixotropy* has also been used. It being remembered that an increase in apparent viscosity τ/D is reflected by a *decreased* slope of the

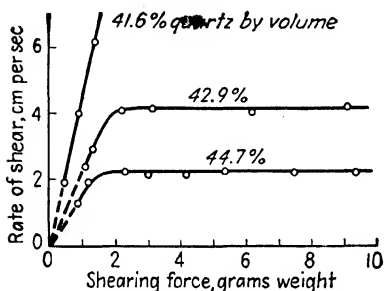


FIG. 7-21. Dilatancy in water dispersions of fine quartz particles. [H. Freundlich and H. L. Roder, *Trans. Faraday Soc.*, **34**, 308 (1938).]

D - τ curve, dilatancy is shown by a bending of the curve toward the shear axis (Fig. 7-21).

Freundlich studied several dilatant systems in which the phenomenon occurred in only a relatively narrow range of high concentrations of the dispersed particles. No yield values were shown by these systems. If the concentration was so low that dilatancy was not observed, the behavior was Newtonian (Fig. 7-21). In these systems he found

that the dilatancy was destroyed if the dispersed particles showed even a slight tendency to adhere to one another.

Freundlich proposed the following mechanism: At low shearing rates the particles in front of the object causing the shear have sufficient time to slip over each other and "get out of the way." At a higher rate of shear they cannot get out of the way fast enough. They pile up and become compressed in front of the shearing object, creating considerable resistance. Behind the shearing object the mass is "stretched." Liquid drains into the larger interstices of this less dense structure, and the mass appears to dry. At the same time this draining of liquid away from the material ahead robs it of lubricant and still further increases the resistance to shear. The independent behavior of the solid particles causes the structure to disappear again as soon as the shearing stress is removed.

Pryce-Jones, Hartley, and others have reported marked dilatancy in systems quite different from those studied by Freundlich; *e.g.*, vinyl resin solutions, 6.5 per cent solutions of calcium naphthenate, and aqueous soap solutions at concentrations as low as 0.02 per cent. They have this in common with the systems studied by Freundlich; below a certain critical rate of shear the viscosity is independent of time, while above the critical

value the "viscosity" increases and continued shearing at a constant rate increases the "viscosity" with time.

While much more quantitative evidence will be needed before all the causes for dilatancy may be stated with certainty, it appears likely that the following phenomena may be involved depending on the particular system: Long molecules may be coiled up or arranged in more or less spherical micelles at low rates of shear but may be straightened or stretched to great lengths at higher rates, thus leading to an increase in apparent viscosity traceable to the hydrodynamic effect. In other high-polymer or colloidal systems, stirring may induce the building up of temporary structures, which disintegrate again on standing or at low rates of shear.

719. Reversible Isothermal Decrease in Consistency with Increased Rate of Shear. Many high-polymer solutions and colloidal dispersions and emulsions set to a gel having a yield value. If sheared by stirring or shaking, they liquefy; but if permitted to stand at rest (zero rate of shear), they gel again. The term *thixotropy* was originally applied to such reversible isothermal sol-gel transformations.

In other cases the materials do not gel on standing. They remain liquid, but on stirring the apparent viscosity falls and then rises again if the rate of stirring is decreased or stirring is discontinued altogether (Fig. 7-22). The term *false body* is often reserved for such behavior, to distinguish it from thixotropy. In many instances whether a system exhibits thixotropy or false body as defined above depends only on the concentration of the dispersed phase or the composition of the solvent in which the solute is dispersed or dissolved. Very general definitions proposed for thixotropy, covering not only the above but related behaviors are "that property of a body by virtue of which the ratio of shear stress to rate of deformation (*i.e.*, τ/D) is temporarily reduced by previous deformation," and "any isothermal reversible decrease in consistency with increase in rate of shear." Some rheologists consider the latter definition too broad since it is based only on equilibrium values and does not differentiate sufficiently between those systems which reach their equilibrium values of consistency rapidly and those which reach them

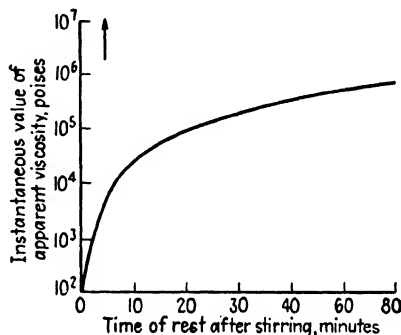


FIG. 7-22. Change in consistency of a paint on standing at rest after stirring. (R. Houwink, "Elasticity, Plasticity and the Structure of Matter," 1940. By permission of The Macmillan Company, publishers, and Cambridge University Press.)

slowly. In this text we shall apply the term *thixotropic effect* to any isothermal reversible decrease in τ/D with increased rates of shear. A thixotropic effect will show itself by a bending of the D - τ curve toward the D ordinate (Fig. 7-23).

Thixotropic effects are manifested by an imposing array of high-polymeric and colloidal systems, among them paints, varnishes, and lacquers; greases; bitumens; gums and starch solutions; gelatin, casein and other protein solutions; clays; inks; soaps; emulsions of many sorts; and blood, plant juices, and other biological fluids. Thixotropic effects are also observed in petroleum and vegetable lubricating oils, especially at high rates of shear and low temperatures.

The importance of thixotropy is aptly illustrated in paints. In a good paint the consistency should be high so that the pigment does not settle out on standing; settled pigment forms a hard mass difficult to stir back into homogeneity. The consistency at the same time should be low so that the paint is not difficult to brush out into a coating of uniform thickness. It must be able to "level"; *i.e.*, the consistency should also be low enough for brush marks (ridges) to disappear (flatten out by flow) before the paint dries. At the same time, the consistency should be high so that the paint will not run when it is laid on a vertical surface (curtaining) or sag or drip off the underside of horizontal surfaces. A nice adjustment of rheological properties is necessary to meet these apparently conflicting requirements. As a matter of fact, they obviously cannot be met by other than a thixotropic system in which both the amount and the rate of the thixotropic effects have been properly adjusted. A good paint, when in a can or bucket, attains such a high consistency (false body or thixotropy) that the dispersed pigment does not settle out inordinately. Indeed, it has been found that, unless the paint is thixotropic, caking troubles are almost certainly encountered. When the paint is sheared by stirring, spraying, or brushing, the consistency drops considerably, making the paint easy to apply and permitting it to level. However, the rate of thixotropic set is such that, although it has time to level, the paint thickens and sets up rapidly enough after application to prevent it from running down vertical surfaces or sagging off the underside of horizontal surfaces.

720. Mechanisms of Thixotropic Change. Some of the mechanisms responsible for thixotropic effects have now been well established. Although many dilute dispersions of essentially spherical colloidal particles obey Einstein's equation, others exhibit apparent viscosities a hundred times higher than that predicted by the hydrodynamical theory. This high consistency is mainly thixotropic, *i.e.*, it disappears at high rates of shear. The effect may be explained by assuming that surface

forces cause the particles to join into filamentous chains, which then mesh into a continuous scaffolding sufficiently strong to impart high consistency or even elasticity and yield value to the system. Stirring or shaking breaks down the scaffolding, and the consistency drops to a more normal value. At rest the particles re-form into chains or a complete scaffolding, and the apparent viscosity again rises.

Dispersions of carbon black in appropriate liquids exhibit thixotropy. In confirmation of the above scaffolding theory it has been found that fine carbon particles associate into filamentous structures (Fig. 13-8) and that gels of carbon black in nonconducting organic solvents conduct the electric current when allowed to stand but cease to do so when the mass is stirred. Filamentous scaffolding structures have been observed under the ultramicroscope in bentonite and other suspensions.

Very dilute solutions of chain polymers are Newtonian liquids. On increasing the concentration, anomalous behaviors are observed. The formation of thixotropic gels is common even at relatively low concentrations. Presumably, continuous scaffolding structures may be formed by association of widely separated polar groups on the chains or by mechanical entanglement of the ultralong molecules. The behavior of raw rubber dissolved in benzene has been described in detail in Sec. 316.

The theory postulates that an elastic scaffolding composed of a relatively few chain molecules anchored at a relatively few points can impart yield value to a mass consisting mainly of solvent molecules, most of which can still wander about in the network with considerable freedom—*e.g.*, a gelatin gel. Such a structure is very close in many respects to that of a rubber. It follows that some gels should exhibit superficially rubbery behavior. This is indeed the case, as evidenced by marshmallow and certain gelatin desserts, to cite two homely examples.

If a solution containing chain polymers is caused to flow, alignment of the chain molecules often occurs. This is detected by the appearance of double refraction in the flowing liquid, which disappears as soon as flow ceases (Sec. 1019). Such alignment in the direction of flow may have several results. There may be a *disentanglement* of the chains and the breakdown of a scaffolding structure, which would lead to a *decrease* in apparent viscosity (thixotropic effect); or the flow may cause an uncoiling and increase in the length and effective volume of the molecules, which would result in a hydrodynamical *increase* in viscosity (dilatancy). It is an interesting fact that certain systems are either dilatant or thixotropic depending on the rate of shear, concentration, and other conditions. Butter, which is a concentrated water-fat emulsion in which milk proteins act as emulsifying agent, exhibits complex behavior. Soft, worked butter remains soft for a considerable time but gradually hardens over the course

of several days (slow thixotropy). In the soft state the effect of strain is primarily to work-harden the system; but if butter that has hardened by long standing is sheared, the first effect of strain is a thixotropic breakdown, which is followed by a subsequent rise in consistency (dilatancy) with further shearing at higher strains.

Some systems that form thixotropic gels possess the property of solidifying more rapidly when sheared (stirred) *very slowly* than when at complete rest. Presumably the very slow stirring acts as an aid to normal

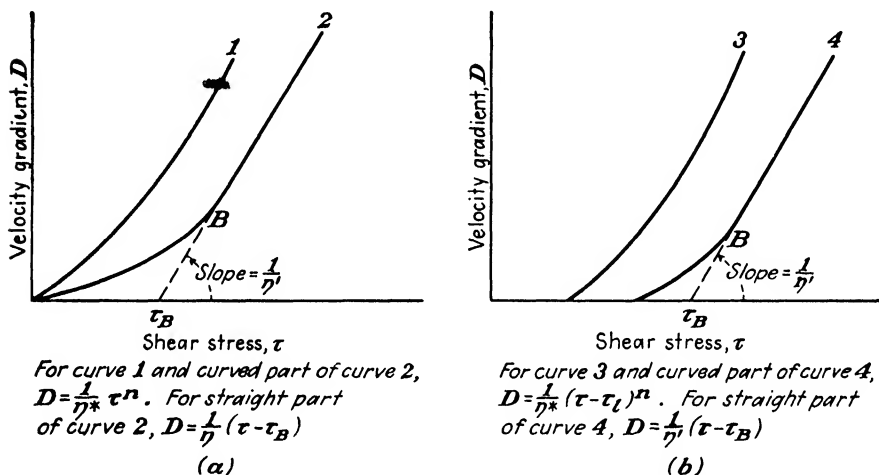


FIG. 7-23. Several types of anomalous flow behavior.

diffusion in enabling the dispersed particles or dissolved chain molecules to arrange themselves into a scaffolding structure. This property is called *rheopexy*. The rheoplectic effect may also be induced by ultrasonic vibrations. Rheopexy is not to be confused with dilatancy. The equilibrium state of the former is a solid gel, while that of the latter is a liquid.

Certain systems, such as asphaltic bitumens, solutions of cellulose esters and ethers, rubbers, boiled starch, and other high polymers, give nonlinear D - τ curves of types 1 and 2, Fig. 7-23a. They are sometimes termed pseudoplastic. Their rheological characteristics are a variable apparent viscosity and the absence of a real yield value. Ostwald referred to them as having "structural viscosity." For some groups of materials, curve 1 and the curved portion of curve 2 are fairly accurately represented by the de Waele-Ostwald formula

$$D = \frac{1}{\eta^*} \tau^n \quad (7-16)$$

Since n is a power greater than 1, the constant η^* does not have the dimensions of a viscosity coefficient. Many other formulas have been proposed.

If the material shows Bingham flow at higher rates of shear (curve 2), the linear portion of the curve is representable by

$$D = \frac{1}{\eta'} (\tau - \tau_B) \quad (7-17)$$

In this case the constant η' has the dimensions of a viscosity coefficient. The extrapolated constant τ_B is sometimes called a yield value even though the system is a liquid (the lower yield value is zero).

Thixotropic effects in materials having finite yield values are shown in curves 3 and 4 of Fig. 7-23b. Analogous equations for these curves are given there. Whether a particular system exhibits a thixotropic effect with sol-gel transformation or without it is often merely a matter of concentration or temperature. A set of curves often encountered in solutions of high-polymer solutes is shown in Fig. 7-24.

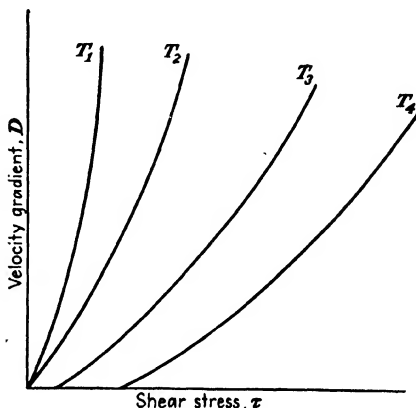


FIG. 7-24. Typical effect of temperature on a thixotropic high-polymer solution. Temperatures decrease in order T_1 to T_4 . Concentration of high polymer is constant.

721. Rate of Thixotropic Change. The rate of thixotropic change as well as its magnitude is important. It is studied in different ways. For example, the material is stirred at a constant rate of shear until a steady state is established, and the shear stress is measured. The material is then allowed to stand for varying periods of time and the shear stress in each instance measured *immediately* upon resumption of stirring *before* equilibrium is reached. Another method is to take a series of stress readings at a set of increasing rates of shear (upcurve) and another series of stress readings at a set of decreasing rates of shear (downcurve), all in accordance with an empirically established time schedule and rigidly standardized experimental procedure. In this way a "hysteresis loop" is obtained, the area of which is a measure of the rate of "thixotropic breakdown" and "thixotropic build-up," from which the rheological behavior of the material may be predicted and controlled.

Pryce-Jones classifies thixotropic materials into three groups in accordance with their behavior when the effect of time is noted.

1. Those whose apparent viscosity τ/D is a function of the rate of shear (decreasing with increasing rate of shear) but is independent of time. In other words, they exhibit a thixotropic effect that is a function of rate

of shear and rate of shear only. (There is no thixotropic hysteresis loop for these systems.) This Pryce-Jones calls *anomalous viscosity*.

2. Those whose apparent viscosity immediately after stirring (shear) has been discontinued is practically independent of the rate of shear but

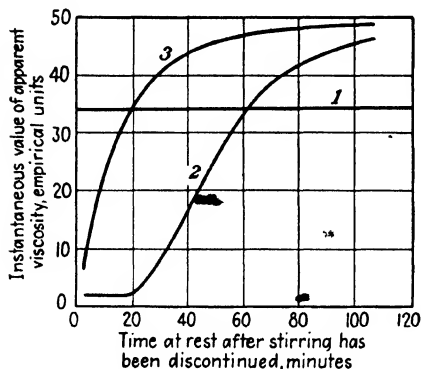


FIG. 7-25. Distinction among anomalous viscosity (Curve 1), thixotropy (Curve 2), and false body (Curve 3). [J. Pryce-Jones, *J. Sci. Instruments*, **18**, 39 (1941).]

whose instantaneous apparent viscosity increases with appreciable rest after stirring. In other words, immediately after stirring, the flow-shear curve of these materials is a straight line, but standing at rest results in an increase in apparent viscosity (instantaneous value), eventually ending in gel formation. Pryce-Jones reserves the term *ideal thixotropy* for this behavior.

3. Those systems whose apparent viscosity is a function of both rate of shear and time of rest after shear. This behavior Pryce-

Jones defines as *false body* with the statement that it is by far the most prevalent type of non-Newtonian behavior.

These differences in behavior are shown graphically in Fig. 7-25.

TESTING PROCEDURE AND EQUIPMENT

722. The consistency of a Newtonian liquid depends only on its viscosity. It is devoid of elasticity or plasticity (under the conditions of test). Since its flow-stress curve is a straight line passing through the origin (Fig. 7-4b), the determination of one point on the curve at one shear stress or driving pressure is sufficient to establish its entire rheological behavior at a given temperature. The consistencies of all other materials may be considered to be composed of both elastic and viscous resistance. The flow-stress plot may pass through the origin but be a curved line (Figs. 7-21 and 7-23a), or flow may take place only when the driving force exceeds a certain minimum (yield) value (Figs. 7-5b and

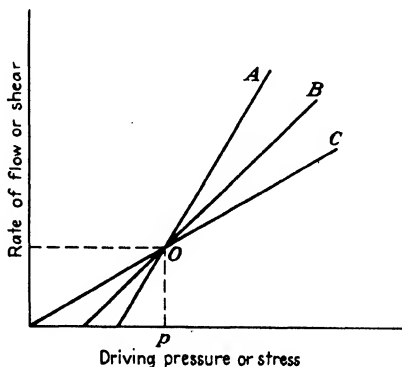


FIG. 7-26. Relations illustrating the inadequacy of one-point determination of rheological behavior.

7-23b). For all such materials, several points on the flow-stress diagram will be required to establish the rheological behavior. Any one-point method of evaluation will obviously be inadequate. For example, three cup greases *A*, *B*, and *C* have flow-stress curves as shown in Fig. 7-26. Assume that they are tested at one driving pressure or stress p corresponding to point *O*, at which they all happen to give the same rate of flow. An investigator, having made this determination, might be misled into the belief that the three greases would give similar results in lubrication practice. Such an assumption could lead to disastrous results since at pressures greater than p the rate of flow of grease *A* is very much greater than that of *C*, whereas at pressures less than p the consistencies of the products are in the reverse order. Owing to failure to recognize this principle, even today one-point methods of evaluation are often applied in "control" work with attendant unsatisfactory results.

It is obvious from Fig. 7-26 that there is no correlation between yield point and apparent viscosity. Grease *C*, like heavy molasses, will flow under its own weight, but increasing the driving pressure will not cause it to flow rapidly. Grease *A*, like mayonnaise, has a yield value and will not flow under its own weight; but once the yield value has been passed, small increases in the driving pressure cause it to flow very rapidly. All possible combinations of yield values and apparent viscosities are found in different materials, as shown below:

Putty:	News ink:
High yield value	Low yield value
Moderate "viscosity"	Low "viscosity"
Mayonnaise:	Lithographic ink:
Moderate yield value	High yield value
Low "viscosity"	High "viscosity"
Pitch:	Gasoline:
Zero yield value	Zero yield value
High viscosity	Low viscosity

Of the rheological instruments widely used in the past many are unsuitable for testing other than Newtonian liquids. This includes outflow-type instruments such as Saybolt viscosimeters and ordinary capillary-tube instruments of the Ostwald type. For one thing, these devices have no convenient means for varying and controlling the shearing stress, relying solely on the weight of the sample itself to supply the driving force. For another, there is no simple means for establishing a steady state, which means that time effects cannot be adequately studied or even detected.

• Among the more suitable instruments are viscosimeters in which a fixed amount of liquid can be subjected continuously to a uniform shearing motion in the annulus between coaxial cylinders or cones and in which

the shearing stress can be varied. One such instrument, the Couette type of rotational viscosimeter, will be described in principle. There is a rotating cup (Fig. 7-27) into which the sample to be tested is placed. A bob is immersed in the material. The bob is suspended from a vertical wire, the upper end of which is firmly clamped to a rigid arm, which is part of the frame of the instrument (not shown). When the cup is

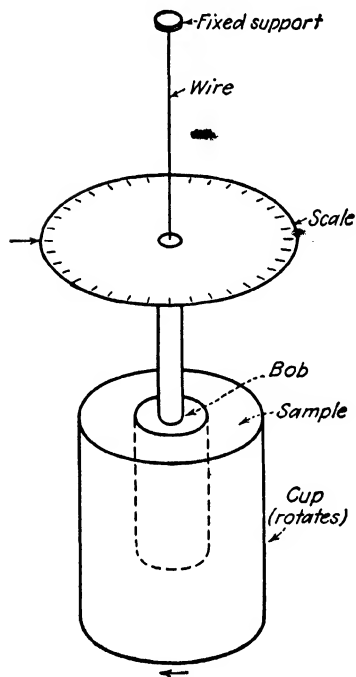


FIG. 7-27. Essential features of the MacMichael viscosimeter, a Couette type.

rotated at a constant speed (by means of a motor), the sample is subjected to shear and owing to its resistance to flow a drag is imposed on the suspended bob, twisting it and the wire through a measurable angle. The instrument can be run as long as is necessary for an equilibrium state to be established. (If the material exhibits thixotropy or false body, the drag on the bob will decrease from an originally high value until the equilibrium value is reached.) At equilibrium, the torque in the wire matches that causing the material in the cup to shear and flow. The angle of twist is read off the scale and from the speed of rotation of the cup and the angle of deflection, the viscosity or apparent viscosity of the material (τ/D) can be calculated. The torque is a measure of the shear stress, τ ; the rate of rotation is a measure of the rate of shear or velocity gradient, D . The speed of rotation of the cup, which is fastened to a motor-driven revolving platform, can

be varied, leading to variation in the torque. By plotting several speeds of rotation against corresponding torques, a flow-shear curve is obtained from which the rheological characteristics of the sample may be deduced. Stirring can be discontinued and the sample permitted to stand for measured periods of time. Instantaneous readings taken on resumption of stirring enable the detection and estimation of the amount and rate of thixotropic build-up.

Even the instrument described above leaves much to be desired. In some models, means for temperature control have been inadequate, and for many purposes the range of rotational speeds has been too limited. Continuously variable speed would be a highly desirable feature.

Couette developed the theoretical equation of flow for a rotational viscosimeter containing a Newtonian liquid.

$$\omega = \left(\frac{T}{4\pi h \eta} \right) \left(\frac{1}{R_b^2} - \frac{1}{R_c^2} \right) \quad (7-18)$$

where ω is the angular velocity, T the torque, h the height of the bob, η the viscosity, R_b the radius of the bob, and R_c the radius of the cup.

This equation may be rewritten as follows:

$$\eta = \frac{TS}{\omega} = \frac{9.55TS}{n} \quad (7-19)$$

where n is rpm and

$$S = \frac{(1/R_b^2) - (1/R_c^2)}{4\pi h}$$

which is a constant for the instrument, to be expressed in cm^{-3} .

Reiner extended this equation to substances exhibiting linear flow over a portion of the curve (Fig. 7-23, curves 2 and 4). The curved portion (below B) presumably exists only where the flow is not completely laminar. The Reiner equation is

$$\omega = \left(\frac{T}{4\pi h \eta'} \right) \left(\frac{1}{R_b^2} - \frac{1}{R_c^2} \right) - \frac{\tau_B}{\eta'} \ln \frac{R_c}{R_b} \quad (7-20)$$

where η' is the pseudoviscosity and τ_B the yield value.

The quantities desired from the experimental measurements are, of course, τ_B and η' . Reiner's equation may be conveniently rewritten as follows:

$$\eta' = \frac{(T - T_2)S}{\omega} = \frac{9.55(T - T_2)S}{n} \quad (7-21)$$

and

$$\tau_B = T_2 C \quad (7-22)$$

where T_2 is the intercept on the torque axis corresponding to τ_B and

$$C = \frac{S}{\ln (R_c/R_b)}$$

which is another instrument constant. These equations cannot be used for nonlinear flow (Fig. 7-23, curves 1 and 3).

Owing to the enormous range of rheological properties exhibited by various materials, no single instrument could be universally applicable. Besides the instruments required for precise scientific instruments, many devices for making rapid empirical evaluations are highly useful in industrial practice (Table 7-9). The latest publications of the A.S.T.M. should always be consulted for standard methods of test.

TABLE 7-9. RHEOLOGICAL INSTRUMENTS AND THEIR APPLICATIONS
(Instruments for measuring rheological properties of gases not included)

<i>Type of Instrument or Test</i>	<i>Examples of Materials to Which Applied</i>
Capillary-tube viscosimeters or plastometers.	Molten chocolate, clays, soils, creams, drilling muds, flour suspensions, greases, honey, paints, pitch, plastics, starch pastes, talc, tar
Jet or orifice viscosimeters. . . .	Oils, butter, cheese, clays, creams, doughs, rubbers, plastics
Rotational viscosimeters (cylinders, cones, spheres, disks, etc.).	Asphalts, bitumens, chocolate, clays, gels, doughs, milk, paints, rubbers, soils, pastes, pitches, high-polymer solutions, emulsions
Falling-ball viscosimeters.	Bitumens, tars, clays, honey, oils; high-polymer solutions, notably cellulose nitrates
Displaced-sphere or disk viscosimeters.	Clays, paints, suspensions and dispersions of many types
Ergometer—bubble extensimeter.	Cheese, doughs, etc.
Farinograph (measures work output during stirring).	Doughs, soils, etc.
Stretching of bands.	Doughs, rubbers, and other highly extensible materials
Compression of materials in bulk.	Cheese curd, soils, road surfaces, etc.
Extension or compression of cylinders, spheres, or strips.	Metals, fibers, plastics, rubbers, rocks, bitumens, butter, cheese, glass, wood
Extension of cylinders under gravity (rheograms).	Doughs, bitumens, etc.
Cutting testers.	Butter, cheese, soap, etc.
Penetrometers.	Bitumens, butter, cement, cheese, doughs, greases, jellies, meats, soils, fruits and vegetables, rubbers, plastics, fibers, woods
Indentation ("hardness") testers.	Metals, plastics, rubbers, wood, minerals, ceramics
Bending and twisting of bars and rods.	Butter, clays, metals, pitch, glass, plastics, wood
Impact testers.	Butter, clays, ceramics, plastics, metals, greases, foundation soils, glass
Resilience (rebound) testers, bouncing balls, damping pendulums, etc.	Doughs, rubbers, road surfaces, glass, plastics
Dynamic fatigue-life testers. .	Metals, rubbers, papers, plastics
Vibration-absorption testers. .	Metals, rubbers, wood, soils, rocks, plastics
Subjective testing by handling	Fibers and fabrics, doughs, bitumens, cheese, curd, rubber

Abstracted from SCOTT-BLAIR, G. W., "A Survey of General and Applied Rheology," Pitman Publishing Corp., New York, 1944.

HIGH-POLYMER SOLIDS

723. Stress-strain Behavior. Ionic crystals, metals, and other low-molecular-weight crystalline solids can be strained only to elongations of 0.1 to 1 per cent before the elastic limit is reached. These small

elastic deformations represent mainly the distortion of normal bond lengths or bond angles.

By contrast, chain-polymeric solids can undergo elastic extensions several orders of magnitude greater (Table 7-7). Chain molecules are capable of extensive coiling or folding. Short small molecules are not. If a particular folded position represents the condition of minimum free energy, the application of external tension can cause temporary straightening and elongation, followed by a return to the original dimension upon subsequent release of the stress, this return being facilitated by thermal agitation and long-range molecular entanglement and anchorage as described in Sec. 516. This radically different kind of elasticity is called *kinetic* or *Mackian elasticity*. Plastics and fibers exhibit elastic deformations of the order of 1 to 10 per cent. In rubbers, the phenomenon attains its peak; reversible elongations of as much as 1,000 per cent are encountered.

There is another important difference between the small "bond-distortion" elastic deformations of low-molecular-weight crystals and the large "chain-straightening" kinetic elasticity of rubbers. Whereas the former does not necessarily involve a change in structure, the latter does. Unstretched rubber is an amorphous mass in the rubbery state; stretched to a 1,000% elongation, it is a crystalline, fibrous material with radically different properties.

If a good Hevea rubber soft vulcanizate is stretched at 20 C to a 700 per cent elongation, the rate of extension and retraction being about 100 per cent per min, the entire deformation is within the elastic limit and the stress-strain curve may be of the type shown in Fig. 7-28.

The first part of curve *OA* is almost linear. In this range, the rubber has an elastic modulus of about 10^6 to 10^7 dynes per sq cm (14 to 140 psi). The extension is due to a gradual uncoiling of the randomly coiled chains. X-ray patterns show there is little or no crystallization during this period.

In the next part of the curve, *AB*, there is a distinct drop in the resistance to extension, the modulus falling to as low as 10^4 dynes per sq cm (0.14 psi). Some internal process appears to be aiding the external stress in producing extension. The internal process in question is crystallization, the explanation being as follows: At the end of *OA*, some of the chains or chain segments have undergone considerable straightening and alignment and are approaching the arrangement they would have in a

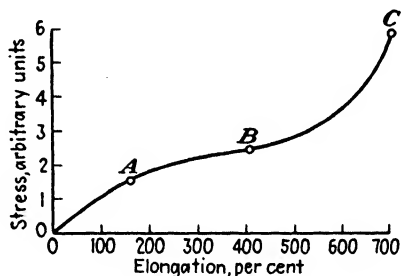


FIG. 7-28. Stress-strain curve of soft vulcanized Hevea rubber (0.5–1.0 per cent sulfur).

crystallite. In this condition they may be considered as crystallization centers. The van der Waals forces between them are sufficient to overcome the small entropy loss involved in their entering a lattice arrangement, which entails further chain straightening and elongation. In other words, at this point the intermolecular attractive forces are aiding the externally applied force in producing elongation so that an increase in length occurs at constant external stress. This is analogous to the action of intermolecular attractive forces during compression of a real gas where a volume decrease takes place at constant external pressure. In both instances a first-order transition occurs, the rubber crystallizing

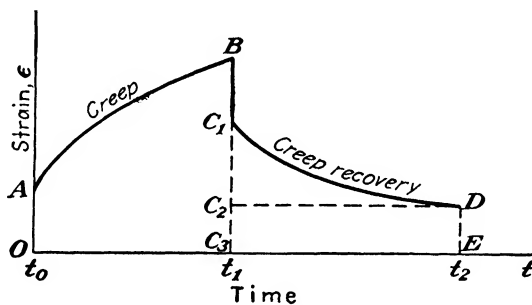


FIG. 7-29. Initial cycle of flow and relaxation typical of many plastics. A stress is applied and held constant from t_0 to t_1 . The stress is then removed and the strain is observed over the interval t_1 to t_2 .

and the gas liquefying. In both instances also, latent heat is evolved, in the case of natural rubber, a heat of crystallization of about 4 cal per g.

Beyond point B, the elastic modulus increases distinctly, attaining values as high as 10^{10} dynes per sq cm (140,000 psi) in the neighborhood of point C. This is to be expected since, in this region, crystallized material predominates. Practically all the stress is now borne by the crystallized phase, and any additional elongation must be gained by stretching the stiff crystallites. X-ray diffraction photographs substantiate this explanation.

724. Relaxation and Creep. A curve typical of those obtained experimentally for the initial flow and relaxation of many plastics is shown in Fig. 7-29. On application of the stress there is an instantaneous elastic deformation OA . This is followed by a retarded deformation (creep) from A to B. On removal of the stress at time t_1 an instantaneous partial recovery BC_1 takes place, followed by a retarded recovery (creep recovery) from C_1 to D at time t_2 . Further recovery after time t_2 is so slight as to be negligible, DE representing a permanent deformation left at the end of the loading-unloading cycle. Figure 7-7, page 266, reveals that this is classified as plastoelastic behavior.

Obviously the creep AB is composed of two components, which become distinguishable only during creep recovery. The elastic component C_1C_2 is recoverable and is termed *primary creep*. Although elastic, primary creep is retarded, and therefore it is unlike the instantaneous action of a steel spring. The nonrecoverable component C_2C_3 (equals DE) is termed *secondary creep*.

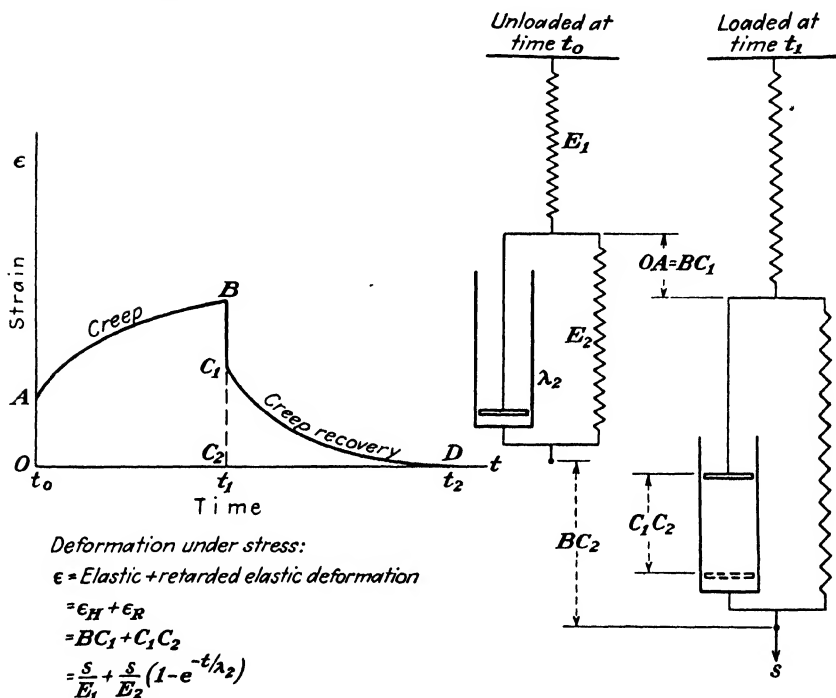


FIG. 7-30. Elastic element in series with a parallel arrangement of an elastic and a viscous element.

It is evident that elastic and viscous properties are reflected in the curve of Fig. 7-29, and accordingly it is profitable to attempt to use mechanical models composed of springs and pistons to explain the behavior. An elastic and viscous element in series is unsatisfactory because a uniform rate of flow is obtained at constant stress [Figs. 7-11a and 7-12a and Eq. (7-12)]. An elastic and viscous element in parallel is also unsatisfactory because no initial elastic deformation is obtained [Figs. 7-11b and 7-12b and Eq. (7-15)].

Figure 7-30 shows an arrangement of an elastic element with modulus E_1 in series with a parallel arrangement of an elastic element with modulus E_2 and a viscous element, the latter combination having the relaxation time λ_2 . The application of a constant external (tensile) stress s produces

an instantaneous elastic deformation OA of the upper spring, which represents an isolated elastic element. Simultaneously the piston and lower spring act in parallel, giving rise to a retarded elastic deformation AB . At any instant t_1 the total deformation BC_2 is the sum of two components—the instantaneous elastic deformation BC_1 (equals OA) and the retarded elastic deformation C_1C_2 (primary creep)—*i.e.*,

$$\epsilon = \frac{s}{E_1} + \frac{s}{E_2} (1 - e^{-t/\lambda_2}) \quad (7-23)$$

On release of the stress the isolated elastic element (upper spring) contracts immediately, resulting in the instantaneous recovery BC_1 (equals OA). The lower spring contracts with a velocity that decreases exponentially to zero owing to the damping action of the viscous element in parallel with it. If one waits long enough after release of the load, no final permanent deformation remains. This arrangement still does not reproduce the curve of Fig. 7-29, for no secondary creep (nonrecoverable flow) takes place.

To arrive at a model that will approach the curve of Fig. 7-29, it is necessary to elaborate the system still further. A variety of combinations of springs and pistons may be put together that will approximate this behavior qualitatively. A widely used model is shown in Fig. 7-31. This differs from the model of Fig. 7-30 in having an additional viscous element. This piston with viscosity η_1 is in series. Application of the external stress s causes this isolated viscous element to flow with a constant velocity s/η_1 , thus producing a permanent deformation. At any instant t_1 the total deformation BC_3 is the sum of three components—the instantaneous elastic deformation BC_1 (equals OA), the retarded elastic deformation C_1C_2 (primary creep), and the viscous flow C_2C_3 (secondary creep)—*i.e.*,

$$\begin{aligned} \epsilon &= \frac{s}{E_1} + \frac{s}{E_2} (1 - e^{-t/\lambda_2}) + \frac{s}{\eta_1} t \\ \epsilon &= \frac{s}{E_1} + \frac{s}{E_2} (1 - e^{-t/\lambda_2}) + \frac{s}{E_1} \left(\frac{t}{\lambda_1} \right) \end{aligned} \quad (7-24)$$

On release of the stress, the isolated viscous element does not move, and thus a permanent deformation DE (equals C_2C_3) is left.

Equation (7-24) does satisfactorily express some deformation data of plastics, and it is sometimes used in the following empirical form:

$$\epsilon = \epsilon_0 + v_0 t - \frac{c}{\alpha} e^{-\alpha t} \quad (7-25)$$

where ϵ is the total deformation, ϵ_0 the instantaneous "elastic" deforma-

tion, v_0 the minimum creep rate, and c and α are constants depending on material, stress, and temperature.

The mechanical model of Fig. 7-31 is not satisfactory even qualitatively for fibers (and their products, yarns, etc.) or mechanically conditioned plastics (see below). The main objection is that in such systems there is often a high degree of reversible elasticity and secondary creep

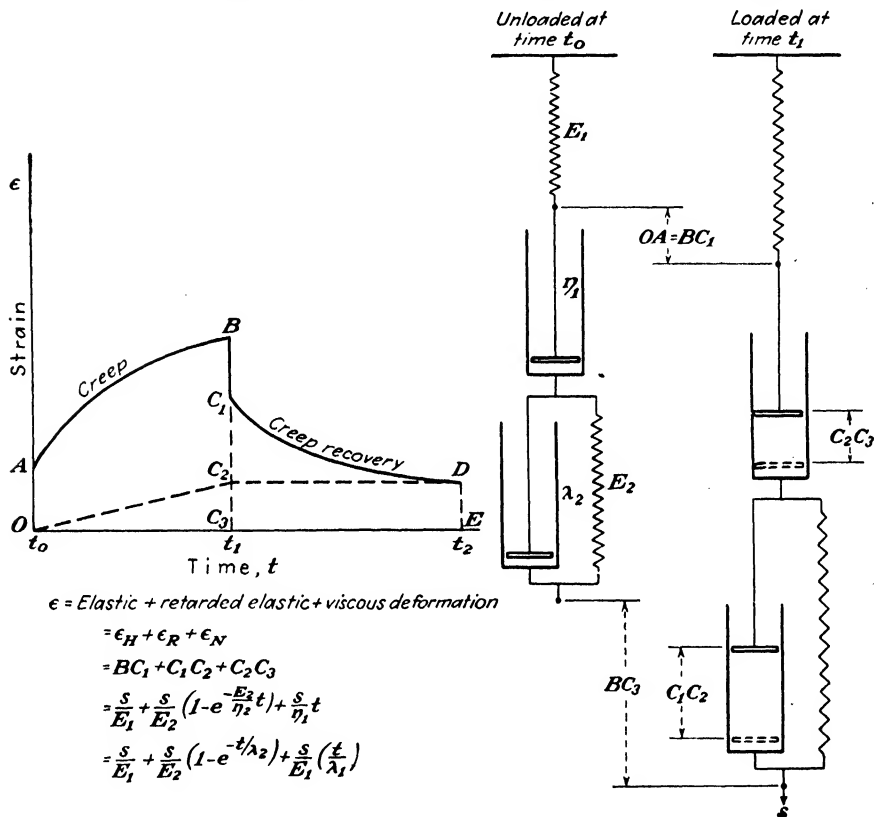


FIG. 7-31. Elastic and viscous elements acting in series and in parallel.

does not occur at stresses below a yield point which is an appreciable fraction of the ultimate strength. Therefore the mechanical model cannot have an isolated viscous element in series. For such systems below the yield point the model of Fig. 7-30 is satisfactory. However, above the yield point, secondary creep takes place, so that some special mechanism inoperative below the yield point must become active. A recently proposed model is more satisfactory.

Let us consider a model containing a viscous element with a ratchet-stop arrangement termed a *blockade*. The blockade allows extension

of the piston when the stress equals or exceeds the yield value. To account quantitatively for the behavior of textile yarns, a spring in parallel with the piston and blockade is necessary (Vreedenberg, 1946). The blockade prevents retraction of the spring. The simplest arrangement of such elements that approximates the flow curve of a fiber is given

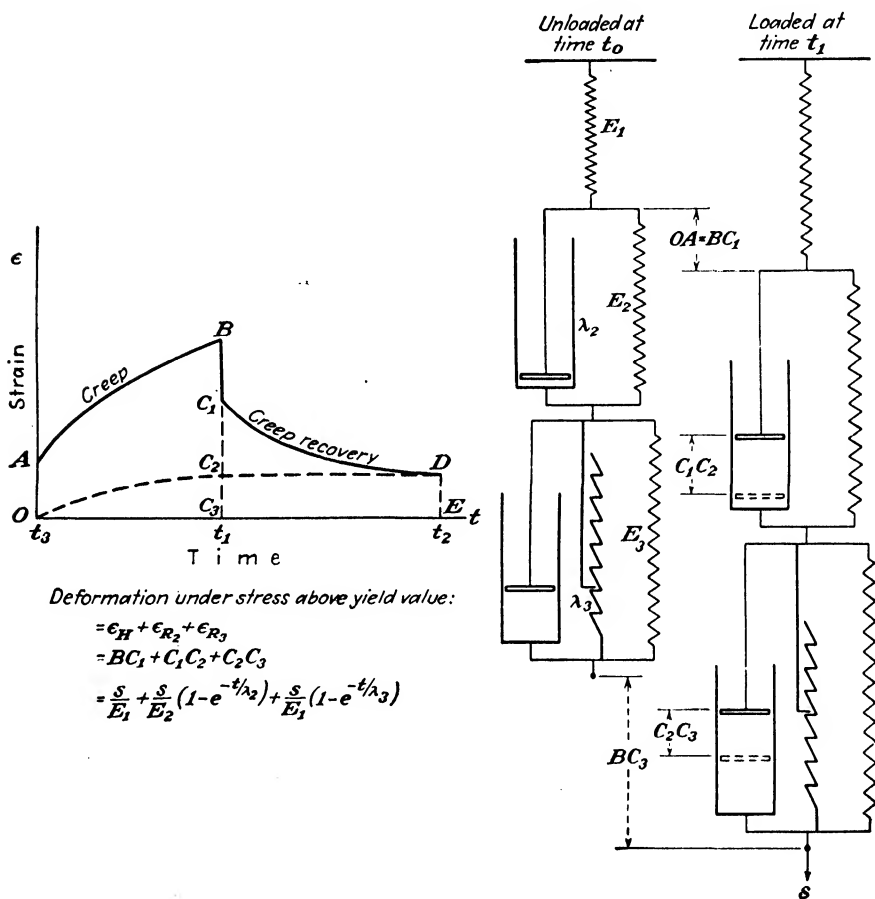


FIG. 7-32. Elastic element in series with parallel arrangements of elastic and viscous elements and a blockade.

in Fig. 7-32. Below the yield value the behavior is identical with the model of Fig. 7-30, only the upper parallel arrangement of piston and spring being active. Above the yield value the blockade is nullified, and the additional retarded deformation of the lower parallel arrangement of piston and spring (elastic modulus E_3 , relaxation time λ_3) become active. At any instant t_1 the total deformation BC_3 is the sum of three components—the instantaneous elastic deformation BC_1 (equals OA), the

retarded elastic deformation C_1C_2 (primary creep), and the blockade retarded deformation C_2C_3 (secondary creep)—*i.e.*,

$$\epsilon = \frac{s}{E_1} + \frac{s}{E_2} (1 - e^{-t/\lambda_2}) + \frac{s}{E_3} (1 - e^{-t/\lambda_3}) \quad (7-26)$$

On release of the stress the blockade sets in, preventing any recovery of the lower retarded spring-piston combination and thus leaving the permanent deformation DE (equals C_2C_3).

The success of mechanical models in depicting the stress-strain behavior of high polymers naturally stimulates the search for plausible molecular structures that have the properties of the parts of the models. These are not difficult to find. Highly crystalline material would have the properties of an isolated spring. Amorphous material of no preferred orientation would have the properties of an isolated piston. Coiled molecules that crystallize on stretching but that spontaneously become disordered again on release of tension (rubberlike systems) would have the properties of a retarded spring-piston combination. Amorphous molecules that crystallize irreversibly on drawing (fiberlike systems) would have the properties of a blockaded retarded spring-piston combination. A finite yield value for the blockade would be due to partial crystallization, *e.g.*, to tensions created during the spinning of the yarn.

Naturally, Eqs. (7-24) and (7-26) cannot be expected to hold exactly. In the first place, they were derived on the assumptions that only a few elastic moduli and a few relaxation times exist in the structural elements and that there is a clear-cut differentiation between elements acting in series and those acting in parallel. Actually, it seems more likely that distribution curves of both exist. Such distribution curves are indeed needed to describe satisfactorily the electrical behavior of high polymers, which also depends on relaxation time (Secs. 1005 and 1006). Furthermore, it is assumed in the construction of the mechanical models that the viscous elements are Newtonian, whereas in fact they are more likely non-Newtonian.

725. Mechanical Conditioning. The flow behavior illustrated in Fig. 7-29 is typical of the *first* loading and unloading cycle of a high-polymer solid. As a consequence of this cycle a permanent set remains. This secondary creep is ascribed in the model of Fig. 7-31 to the flow of the viscous element in series and in the model of Fig. 7-32 to extension of the blockaded system. On repeating the cycle there may or may not be further secondary creep, but if so it is less than during the first cycle (Fig. 13-11, page 575). In subsequent cycles less and less additional permanent set is observed. The number of cycles required to eliminate completely further secondary creep varies from 1 in high-tenacity fila-

ments to 10 or more for rubbers. This behavior is fully accounted for by models of the types of Figs. 7-31 and 7-32 in that, the series viscous elements having flowed and the blockaded systems having been extended in the early deformations, no further flow mechanism is present.

This phenomenon finds application in experimental studies and in practice. If the high-polymer solid is given a number of loading and

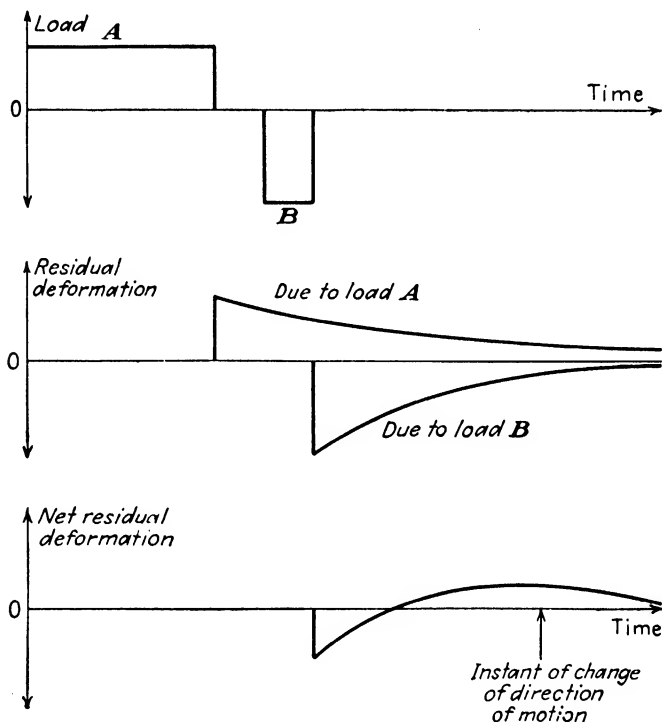


FIG. 7-33. Reversal of direction of creep recovery due to superposition of opposing residual deformations. (H. Leaderman, "Elastic and Creep Properties of Filamentous Materials and Other High Polymers," Textile Foundation, New York, 1943.)

unloading cycles before being used, subsequent secondary creep is eliminated and the member has become dimensionally stabilized, its behavior then becoming qualitatively like that shown in Fig. 7-30. Such treatment is termed *mechanical conditioning*. It is important that the load used in the mechanical-conditioning cycles be at least as high as any future expected load. If a future load exceeds that used during mechanical conditioning, additional secondary creep will take place.

726. Superposition of Creep. Primary creep and recovery are highly time-dependent phenomena; *e.g.*, the longer the time after unloading, the greater the fraction of creep recovered. If a body is subjected to a

number of loadings and unloadings, complex creep phenomena may take place. These are reduced to a simple scheme by the *superposition principle* proposed by Boltzmann. This principle states in effect that the deformation at any instant of a body manifesting primary creep is due not only to the load acting at that instant but also to the entire previous loading history and that the deformation is the summation of the deformations due to each separate loading action.

By choosing properly the relative magnitudes of the loads and their durations it is possible to demonstrate this principle in a striking manner. Figure 7-33 represents such a demonstration on a mechanically conditioned body. The top diagram represents a load A applied in one direction for a long time and removed and then a load B applied in the opposite direction for a shorter time and removed. The middle diagram represents the individual residual deformations due to these two loads. The bottom diagram represents the course of the net residual deformation. There is first a negative residual deformation, which gradually disappears, and a positive deformation then appears. Creep recovery thus takes place first in one direction; the motion of the body ceases and then reverses its direction, and recovery then takes place toward the final equilibrium position.

This dramatic phenomenon is sometimes termed the *memory effect*. Kohlrausch, who first produced this effect using rubber specimens, stated: "To my knowledge there are only a few processes as remarkable as this spontaneous change of direction of motion of an inanimate object."

THE INFLUENCE OF TEMPERATURE

727. The flow properties of materials are strongly dependent on temperature, viscosity decreasing rapidly as the temperature increases (Fig. 7-18). The temperature functions are of the Arrhenius type (Secs. 229 and 230), indicating that the controlling factors are activation processes. Thus, the viscosity-temperature relation of a liquid may be expressed either as

$$\phi = Ae^{-U/RT} \quad (7-27a)$$

or

$$\eta = Be^{U/RT} \quad (7-27b)$$

As previously stated, in a liquid there is continuous Brownian movement, permitting molecules to slip from one configuration to another. In a flowing liquid those configurations will be favored which are able to relax the applied stresses. However, only molecules that, during collision, have received energy in excess of the average energy (activated molecules) will be able to migrate from one configuration to another and relieve stress. Eyring has related the activation energy to the heat of

vaporization: the ratio of heat of vaporization to activation energy of flow should be 3 for a spherical-type molecule and 4 for an unsymmetrical chain-type molecule. These theoretical ratios have been found to hold fairly well.

In plastic solids the rate at which cohesive flow of chain segments past one another takes place is similarly given by an exponential function

$$\lambda = Be^{U/RT} \quad (7-27c)$$

Table 7-10 gives some values of activation energy for primary creep. (The dynamic method is described in Sec. 953.)

TABLE 7-10. ENERGY OF ACTIVATION FOR PRIMARY CREEP

Material	Method	U , kcal/g mole
Glass.....	Recovery	5.8
Silver.....	Recovery	11.0
Iron.....	Creep	19.5
Hevea rubber, soft vulcanizate.....	Creep	39.0
Bakelite.....	Creep	80.0
Hevea rubber, hard vulcanizate.....	Creep	97.0
Hevea rubber, soft vulcanizate.....	Dynamic	37.6
Chloroprene, soft vulcanizate.....	Dynamic	39.0
Methyl methacrylate, unplasticized.....	Dynamic	72.0
Methyl methacrylate with 10% plasticizer..	Dynamic	57.8
Methyl methacrylate with 20% plasticizer...	Dynamic	52.0

LEADERMAN, H., "Elastic and Creep Properties of Filamentous Materials and Other High Polymers," Textile Foundation, New York, 1943.

Examination of Table 7-10 indicates that activation energy increases with firmness of bonding and cross-linkage and that it decreases with addition of plasticizer. These effects are in harmony with the usual behaviors.

Theoretically, each relaxation mechanism should have its own activation energy; accordingly, the activation energy furnishes valuable information as to the relaxation mechanism. If U is constant (Fig. 10-10), the relaxation mechanism does not change with temperature. If U changes sharply (Fig. 13-15), an abrupt change in mechanism occurs. A nonlinear relation between logarithmic rate and reciprocal temperature will be due to a continuous change of mechanism.

Mechanical failure of solids is also temperature dependent. The yielding of the bond between two molecules requires activation. Theoretical considerations lead to the following particularly noteworthy equation relating the ultimate tensile strength of brittle solids with the

duration of application of stress:

$$t = Be^{EU/sRT} \quad (7-28)$$

where t is the time for fracture, E Young's modulus, and s the fracture stress.

This equation is in accord with the discussion of Secs. 706 and 711 *ff.* It has been shown to be valid for glass over a time factor of 10^7 . Owing to the exponential character of this equation, the time varies extremely steeply with the stress. A reduction of 30 per cent in the stress increases the duration more than five hundredfold.

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See also Appendix A.

PARTICULAR TOPICS

See references accompanying tables and figures of this chapter.

Molecular Theory and Rheological Behavior of Solids

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Rheological Behavior of Low-molecular-weight Liquids

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Creep of High-polymer Solids

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CHAPTER 8

MOLDING AND MANIPULATION

As with all materials of construction, the utility of a high polymer depends to a great extent upon the molding and fabrication processes to which it lends itself. These in turn are governed primarily by its rheological behavior, *i.e.*, whether it is nonmoldable, thermoplastic, or mutaplastic. It is the object of this chapter to present briefly the types of auxiliary materials employed in the production of plastic artifacts and the principal methods of molding. Factual knowledge of these phases of the subject leads to a broader understanding of the theoretical and developmental problems facing the high-polymer industries.¹

MIXES

800. It is unusual for a finished high-polymer article to consist solely of high-polymer molecules. Usually the material fed into the manufacturing equipment is an intimate mixture of 4 to 10 ingredients, each of which either discharges a useful function during molding or imparts some useful property to the finished artifact. This is the *mix*. A mix used for molding is called a *molding compound*; one that is to be vulcanized, a *vulcanizing mix*. A liquid or emulsion mix is often called a *dope*, while those used for surface coatings are known as *paints*, *varnishes*, and *lacquers*.

The materials of the mix other than the plastic high-polymer constituents are usually referred to as *compounding ingredients*, while the high-polymer constituents are known as *binders*. The nature and relative proportions of the compounding ingredients are varied to meet a multiplicity of molding problems and to impart a wide range of properties to thousands of finished products. Typical commercial mixes are shown in Tables 8-1 and 14-3.

TYPES AND FUNCTIONS OF COMPOUNDING INGREDIENTS

The main types of compounding ingredients and their functions are described below. For detailed discussions of these materials, the reader is referred to books devoted to the technology of particular branches of

¹ The handbook published by the Society of the Plastics Industry is a particularly valuable reference for practical information and know-how relating to plastics and merits special mention.

high-polymer industry. Appropriate references will be found in Appendix A and at the ends of chapters of this text.

801. Binders. The binder, or binding polymer, is the material that acts as the matrix which ultimately cements the ingredients of the mix

TABLE 8-1. EXAMPLES OF HIGH-POLYMER MIXES
Automobile Tire-tread Mix (Ready for Vulcanization)

Ingredient	Type	Parts by wt
Rubber.....	Binder	100
Carbon black.....	Reinforcing filler	50
Sulfur.....	Vulcanizing agent	0.5-3.5
Accelerator.....	Catalyst	0.5-1.5
Zinc oxide.....	Activator	1-10
Stearic acid.....	Activator	0.5-2.0
Pine tar.....	External plasticizer	3
Antioxidant.....	Aging inhibitor	0.25-1.5

Thermosetting Molding Compound (Ready for Compression Molding)

Ingredient	Type	Wt %
Phenol-aldehyde resin.....	Binder	43.0
Wood flour.....	Filler	51.0
Hexamethylenetetramine.....	Catalyst; hardener	3.7
Black dyes and pigments.....	Coloring materials	1.5
Metallic soap.....	Lubricant	0.8

Thermoplastic Molding Compound (Ready for Injection Molding)

Ingredient	Type	Wt %
Cellulose acetate.....	Binder	74.6
Diethyl phthalate.....	External plasticizer	24.8
Carminc red.....	Coloring material	0.4
Montan wax.....	Lubricant	0.2

Dope for Making Transparent Film (Ready for Casting)

Ingredient	Type	Wt %
Cellulose acetate, medium viscosity.....	Binder	15
Triphenyl phosphate } Dimethyl phthalate }	Permanent external plasticizers	{ 2 3
Acetone } Alcohol } Methyl Cellosolve }	Solvents, thinners, temporary plasticizers	{ 60 10 10

TABLE 8-1. (Continued)
Long-oil Quick-drying Varnish Mix (Ready for Cooking in Kettle)

Ingredient	Type	Amount
Tung oil.....	Binder (after varnish has dried)	30 gal
Limed rosin.....	Binder modifier	106 lb
Litharge.....	Catalyst (drier)	6 lb
Magnanese resinate.....	Catalyst (drier)	2¾ lb
Mineral spirits, added at end of cook.	Solvent, temporary plasticizer	80 gal

Emulsion-form Fabric-backing Compound (Ready for Applying and Vulcanizing to Fabric)

Ingredient	Type	Parts by wt
Neoprene, stabilized latex, 50% solids.....	Binder	100
Zinc oxide.....	Accelerator and filler	25
Natural whiting.....	Filler	25
Neozone D (antioxidant).....	Aging inhibitor	3
Water glass.....	Activator	0.25
Casein.....	Thickener	0.5
Aquarex D.....	Surface-active agent	0.25
Water.....	Vehicle	100

Wood Adhesive (Ready for Application and Bonding)

Ingredient	Type	Parts by wt
Urea-aldehyde resin.....	Binder	100
Wheat flour.....	Extender (filler)	100
Ammonium chloride.....	Catalyst	10
Water.....	Vehicle	130

into a cohesive finished article. It must always be of such character that it is capable of exhibiting continuous flow, at least until the artifact has been formed. It is generally the most important constituent, and the finished artifact is usually "typed" after it. Thus, one speaks of "rubber" tires, "tung-oil" varnishes, and "cellulose nitrate" lacquers regardless of the other ingredients that may be present.

Thermoplasts may be introduced into a mix in fully polymerized form. Thermosetting materials, on the other hand, must be introduced as functional, essentially linear polymers that undergo chemical change to the less soluble, less fusible state during manipulation.

802. Fillers and Extenders. A *filler* is a material, usually nonplastic and insoluble, added expressly to impart to the finished article desirable mechanical, chemical, or electrical properties not possessed by the binder itself. (In this text a differentiation will be made between fillers as above defined and extenders or diluents, which are materials added solely to cut material cost.)

Fillers are more widely used in conjunction with mutaplasts, whereas permanent external plasticizers are more extensively employed with the thermoplasts.

Fillers are usually employed in sizable weight percentages. Those which enhance mechanical strengths are called *reinforcing fillers*. The carbon black added to a natural rubber tire tread mix may bring about a 40 per cent increase in tensile strength and a greatly enhanced abrasion resistance. The relatively low impact strengths of "pure" heat-hardened phenol-aldehyde resin is improved notably by the addition of 50 per cent or more of cellulosic fillers such as shredded rags, cotton flock, or laminations of paper, fabric, or wood. Highly purified celluloses are used with the urea and melamine resins where it is essential to preserve translucence and color range. At the same time that the mechanical properties are improved, the material cost is often decreased, since many fillers are less expensive than the binders.

Asbestos and mica are added to thermosetting resins to impart higher heat resistance and better electrical characteristics rather than to reinforce the binder. Woven glass fabric performs the same functions and reinforces as well. These are the most important inorganic fillers.

Powdered slate, pumice, China clay, gypsum, and infusorial earth are inorganic fillers incorporated into mutaplasts where hardness is more important than mechanical strength.

Over and above the ability to impart some particular desired property to the finished article, the following attributes are often sought in a filler: (1) low cost; (2) low specific gravity; (3) ease of preparation; (4) ease of compounding into mix; (5) ability to improve preforming and molding qualities of the mix; (6) freedom from abrasive action or chemical attack on molding or mixing equipment.

The physical state of subdivision of a filler is often of outstanding importance. For instance, before carbon particles will act as a reinforcing filler for natural rubber, they must be in the colloidal range of fineness. Larger particles are either only semireinforcing or inert. But perhaps the best illustration is afforded by cellulose used in conjunction with phenolic resin. From Table 8-2 it is evident, for example, that wood added in ground form (wood flour) produces no notable improvement in ultimate tensile strength or elastic modulus, whereas wood added in the

form of thin, stacked sheets (wood veneers) brings about a marked increase in tensile strength and a thirtyfold improvement in Young's modulus. It will be seen, furthermore, that cellulose in the form of canvas or light

TABLE 8-2. EFFECT OF FILLERS ON PHENOL-ALDEHYDE PLASTICS

Filler	Ultimate tensile strength, psi	Elastic modulus in tension ($\times 10^{-6}$) psi	Relative impact strength	Dielectric strength, short time, volts/mil. $\frac{1}{8}$ in. thickness	Continuous operating temperature, deg F	Water absorption, 24 hr, %
None. Straight phenol-aldehyde resin	7,500	0.8	1	450	250	0.15
Wood flour	7,500	1.0	1.3	400	300	0.40
Shredded fabric	7,500	0.9	6	350	250	1.20
Paper laminations, Grade X*	12,500	1.2	10	750	250	2.0
Canvas laminations, Grade C*	9,500	1.0	20	200	250	0.5
Lightweight fabric laminations, Grade L*	9,000	1.0	20	200	250	0.5
Birchwood veneers (plastic plywood)	27,700	3.4	12			
Asbestos	7,500	0.3	2	250	450	0.15
Glass-fabric laminations	17,000	1.5	20	600	480	0.4

* Designations of National Electrical Manufacturers' Association (N.E.M.A.) and American Society for Testing Materials (A.S.T.M.).*

fabric laminations is most effective in improving impact strength. Whereas unfilled phenol-aldehyde is entirely too brittle for most purposes, when filled with fabric laminations it can be used for making silent, heavy-duty, abrasion-resistant gears of 5 ft diameter and 10 in. face. These gears are nonsparking and noncorroding and are lubricated by water instead of oil. They are only one-sixth as heavy as steel gears and the material may be machined much more readily.

Specific correlations of filler to intended use of the finished artifact are presented in Table 8-3.

803. External Plasticizers. External plasticizers are added to mixes for two main reasons: (1) to aid in compounding or molding; (2) to modify the properties of the finished product.

As an example of the former, one may cite the addition of pine tar to raw rubber to reduce the time and power required to break the rubber down into a sufficiently soft, plastic mass to permit the incorporation of

TABLE 8-3. MOLDED PLASTICS AND RELATION OF FILLERS TO APPLICATIONS

Binding polymer	Filler	Characteristics displayed to best advantage	Typical examples
Urea-aldehyde.....	Purified wood pulp: alpha-cellulose	Appearance. Translucence and pastel colors	Handles. Housings for clocks. Radio cabinets. Lighting globes
Phenol-aldehyde....	Wood flour, vacuum-dried	Electrical qualities	Ignition-coil housings
Phenol-aldehyde....	Wood flour	Fair all-round properties. Excellent moldability	Bottle caps, housings, containers, handles, gadgets of many kinds
Phenol-aldehyde....	Fiber cotton	Good impact strength. Excellent surface finish	Handles for high-grade instruments, telephone handsets
Phenol-aldehyde....	Shredded fabric	Higher impact strength	Goggle frames, small gears, couplings, instrument cases
Phenol-aldehyde....	Canvas laminations	Outstanding impact strength	Pulleys, heavy-duty gears, corrosion-resisting pump parts and housings
Phenol-aldehyde....	Wood veneers	High structural strength	Plastic plywood for furniture, paneling, doors, aircraft members
Phenol-aldehyde....	Asbestos	High resistance to heat and chemicals	Chemically resistant storage tanks, containers, ash trays, switch insulation, plugs, housings for heating units
Phenol-aldehyde....	Mica	Low-loss electrical properties	Coil forms, terminal blocks, condenser housings for radio units
Phenol-aldehyde....	Graphite	Lubricating properties	Self-lubricating bearings

carbon black, zinc oxide, and other compounding ingredients into the vulcanizing mix. The addition of tricresyl phosphate to polyvinyl chloride to attain "rubberiness" affords a good instance of the second function (Table 3-2, page 84).

Since external plasticization is fundamentally a solvent action, it is understandable why external plasticizers are used often and in large

amounts with polymers of the thermoplastic type. Occasionally, however, these materials are added to a thermosetting or otherwise mutaplastic mix, most often to increase plasticity during molding or manipulation rather than to effect major modifications in the properties of the finished product.

Besides the fundamental requirements of compatibility and nonvolatility, other properties often desired in a permanent external plasticizer are

1. Freedom from odor, taste, and toxicity when used in such articles as wrist-watch straps, belts, or refrigerator trays
2. Stability to the atmosphere so that its chemical character and effectiveness will not alter
3. Resistance to water or other specific solvents so that it will not be leached out or hydrolyzed
4. Ability to impart nonflammability when used with cellulose nitrate and other inherently flammable polymers
5. Ability to improve adhesion in the case of plasticizers added to lacquers and other surface coatings
6. Water-whiteness and light stability if transparent objects are to be produced

A table of plasticizers is given in Appendix E.

804. Catalysts, Inhibitors, and Promoters. Where it is required that a chemical reaction accompany the molding or manipulation of a mix, a catalyst is usually incorporated. The molding of thermosetting phenol-, urea-, and melamine-aldehydes and the vulcanizing of rubber involve cross-linkage reactions *in the mold*. Catalysts are added to speed up these reactions. The "drying" of linseed and tung oils in oleoresinous varnishes involves polymerization reactions, and catalysts are also incorporated into these products. Cast methyl methacrylate is made by prepolymerizing the monomer to the point where it is a viscous, sirupy liquid, mixing it with an adequate amount of catalyst, and pouring this into an open, heated mold, from which it is ejected after the contents have polymerized to the solid state.

Special names are applied to catalysts used in various branches of high-polymer technology. Thus, those used in the molding of thermosetting plastics are sometimes termed *hardeners*; those incorporated into oleoresinous varnishes are called *driers*; and rubber-vulcanization catalysts are known as *accelerators*.

In some instances, notably addition polymerizations involving the olefinic bond, the monomers can join to one another in more than one way. When such is the case and one reaction mechanism is preferred to another, recourse is had to the use of *orientation catalysts*, which, as the

name implies, are catalysts that promote the preferred reaction at the expense of the others. Orientation catalysts find important applications in synthetic rubber and phenol-aldehyde resin manufacture.

Catalysts are, of course, extensively employed in the manufacture of monomers from basic raw materials, as well as the subsequent formation of polymers from their monomers.

The polymerizations of phenol-, urea-, and melamine-aldehydes are catalyzed by various electrolytes, prominent among them being sulfuric acid, ammonia, and salts. Sulfuric acid is employed to catalyze the acetylation of cellulose. The polymerization of vinyl and related compounds is catalyzed by oxidizing catalysts, notably benzoyl peroxide. These latter catalysts may also be used in conjunction with the alkyd resins. Organic salts of cobalt, manganese, and lead are prominent among the paint and varnish driers. The most important vulcanization accelerators are derivatives of carbon disulfide, *e.g.*, thiuram sulfides, dithiocarbamates, thiazoles, and thiazolines.

Inhibitors, or *negative catalysts*, are sometimes added to the mix. Vinyl chloride and vinylidene chloride polymers show a tendency to undergo decomposition and discoloration when raised to the temperatures required for commercial molding. The inhibitors that prevent this are called *heat stabilizers*. Heavy metal stearates have been used for this purpose with polyvinyl chloride. Certain aralkyl ethers, prominent among them being *bis- α* -phenylethyl ether, act simultaneously as heat stabilizers and external plasticizers for vinyl chloride and vinylidene chloride polymers.

Negative catalysts added to rubber mixes to prevent premature vulcanization in the compounding equipment are known as *accelerator retarders*. They are occasionally required to prevent prevulcanization when very powerful accelerators are employed. Certain organic acids such as benzoic, salicylic, and phthalic have been found effective. Another type of inhibitor added to rubber goods is the *aging retarders*. These materials prevent deterioration of rubber goods, presumably by inhibiting oxidation.

Inhibitors are also used to prevent the premature polymerization of monomeric materials during storage prior to use. Vinyl and diene monomers are outstanding offenders in this regard. Oxidation inhibitors are usually added. Tannic acid, hydroquinone, and aromatics containing phenolic and amino groups are employed for this purpose. To be considered effective in the commercial sense, the inhibitor must prevent prepolymerization when added in amounts no greater than 0.01 to 0.02 per cent.

Not all catalysts used with high polymers are simple. Catalyst

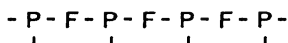
activators, or *promoters*, must sometimes be added before the catalyst exercises its maximum effect. In the rubber industry, these promoters are known as *accelerator activators*, and those commonly used are metal oxides and aliphatic monocarboxylic acids. Organic salts of lead, manganese, and cobalt are increasingly effective as varnish driers, in the order named. But a mixture of these salts is a more effective catalyst than any one alone.

Catalysts should be chosen not only for their effectiveness in accelerating and directing the course of the desired reaction but also with an eye toward their effect on the properties of the finished product. For example, an electrolyte used as catalyst will lower the dielectric qualities of the finished material.

805. Cross-linking Agents. Cross-linking agents are materials added to a mix to bring about space polymerization by reacting with a functional binding polymer. The term leaves something to be desired since in some cases what are presumed to be cross-linking reactions are actually in doubt. As will be readily understood, cross-linking agents are used only in potentially polyfunctional systems.

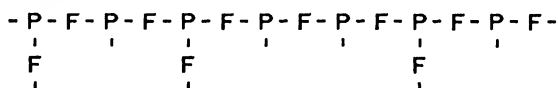
Assume that one starts with a polyfunctional system composed of a trifunctional monomer, $\begin{array}{c} | \\ -P- \end{array}$, and a bifunctional monomer, $-F-$. If it is desired to attain a space-polymerized finished product, the system may be handled in either of two ways.

Method A. React 1 mole of $\begin{array}{c} | \\ -P- \end{array}$ with not more than 1 mole of $-F-$ under conditions favoring the formation of linear polymers. The product will then be essentially



If this functional linear polymer is then used as a binding polymer, more of reagent $-F-$ must be added to the mix in convenient form if a space-polymerized end product is to be attained. This last added portion of $-F-$ will be a typical cross-linking agent.

Method B. React 1 mole of $\begin{array}{c} | \\ -P- \end{array}$ with more than 1 mole of $-F-$ under conditions that do not permit any appreciable cross-linkage to take place. The reaction product may then be represented by



If this material is used as a binding polymer, the individual chains will be capable of cross-linkage without the necessity of further addition

of —F—. In other words, in this instance, the cross-linking agent has already been added during preparation of the binding polymer and does not have to be incorporated into the mix as a special ingredient.

The cross-linking agents employed in conjunction with thermosetting plastics are often called *hardening agents*. Hexamethylenetetramine (hexa) and paraformaldehyde are among those added to phenol-aldehyde and urea-aldehyde molding mixes. The cross-linking agents used with rubber are called *vulcanizing agents*. Sulfur is the most prominent among them.

In some instances a special type of cross-linking agent that also serves as external plasticizer is used. This is termed a *vulcanizing plasticizer* (Sec. 1303).

806. Lubricants. Lubricants are used to prevent molded pieces from sticking to the mold. They may be either incorporated into the mix or applied directly to the mold surfaces. Different lubricants work best with different mixes, and at present a choice of lubricant is mainly a matter of trial. Silicone oils have been found unusually effective in many cases.

Oils, waxes, petrolatum, fatty acids, and soaps are often applied sparingly with a brush or spray. Carnauba wax and graphite, dusted on the surfaces, are often used specifically while breaking in a new mold.

When the lubricant is added as a compounding ingredient, it is usually used in amounts less than 2 per cent and most often less than 1 per cent. The lubricant should be incompatible with the rest of the mix. It should not be absorbed but should stay on the surface of the particles of the molding powder as a fine film. It must not cause spottiness on the surface of the finished piece.

807. Solvents. Solvents may discharge several different important functions in high-polymer mixes. They may be used as dispersing media to obtain uniformity in the mix or added to act as *temporary* external plasticizers. They may be employed as thinners to reduce the viscosity to a suitably low working value, or they may play the role of swelling agents.

The thinning of lacquers and varnishes so that they may be brushed or sprayed, the dampening of fabrics with water during ironing, the "plumping" of leather hides with aqueous solutions of electrolytes, and the moistening of the hair before combing are representative illustrations of solvent functions.

Important aspects of solubility phenomena have been discussed in Chaps. 3 and 6. Mixed solvents and single solvents containing more than one type of functional group are often employed in order to obtain maximum solubility. Solvents are selected to attain controlled rates of

TABLE 8-4. GENERAL PROPERTIES OF COLORING MATERIALS USED IN PLASTICS

Type	Affinity	Hue	Dispersibility in resins	Fastness properties			Uses
				Heat	Light	Alcohol and water	
Acid dyes.....	Direct for pro- teins	Bright and strong	Generally poor, varies with dye and conditions	Moderate	Good	Bleed	Protein plastics, cast phenolics, amino resins, water-soluble binders
Mordant dyes..	Direct for pro- teins	Some- what dull	Generally poor	Moderate	Very good	Bleed	Same as acid dyes
Basic dyes.....	Proteins, certain clays, high tan- ning cellulosic materials	Very bright and strong	React with many resins. Good	Moderate. Some reds good	Poor	Bleed	Can be applied to most plastics. Not much used in the hydro- carbon products
Direct and de- veloped dyes.	Cellulosic mate- rials	Some- what dull	Generally poor	Moderate	Moderate	Bleed	Used to color cellulosic fillers and water-soluble binders. Useful in beater-dyed paper panel stock
Sulfur dyes.....	Cellulosic mate- rials	Dull	Poor	Moderate	Good	Good	Used chiefly for rubber tire fabrics and trubenized cloth
Vat dyes.....	Cellulosic mate- rials	Some- what dull and weak	Moderate unless specially proc- essed	Moderate	Very good	Good; bleed in hydro- carbons	Useful in many plastics but expensive
Acetate dyes....	Cellulose acetates	Bright	Moderate	Good	Moderate to good	Bleed	Cellulose acetate fabrics, sheets, and fabricated pieces

TABLE 8-4. (Continued)

Type	Affinity	Hue	Dispersibility in resins	Fastness properties			Uses
				Heat	Light	Alcohol and water	
Toners and lakes. Inorganic pig- ments.	All materials by adhesion	Bright	Good	Good to moderate	Moderate to good	Many bleed	All types of plastics
	All materials by adhesion	Soft- toned, dull	Good	Good	Very good	Good	All opaque plastics
Spirit-soluble dyes.	All materials by absorption or adhesion	Bright and strong	Good	Varies	Varies. Some are good	Bleed	Most plastics that tolerate alcohols or glycol ethers in processing
Oil-soluble dyes.	All materials by absorption or adhesion	Bright and strong	Good	Good	Moderate, depends on the medium	Bleed	Resins, cellulose esters, and hydrocarbon plastics. Usu- ally not fast to light in cellu- lose nitrate. Act as anti- oxidants, inhibiting peroxide catalysts

PLASTICS CATALOGUE CORP., "Modern Plastics Encyclopedia," New York, 1947.

evaporation when this is important in determining the mechanical properties or degree of orientation of the polymeric molecules in surface coatings or cast films. A table of solvents is given in Appendix E.

808. Coloring Materials. Color appeal is often a prime consideration in high-polymer artifacts such as molded products and surface coatings. In other cases, complete transparency and water-whiteness are the goal. If a high polymer can be produced in transparent, water-white form, it is free of color limitations; *i.e.*, it may be produced in any transparent shade by the incorporation of soluble dyes or in any opaque color by the use of pigments or a combination of dye with opaque pigment or filler. Many of the cellulosic derivatives and the vinyl type of polymers are water-white or nearly so. Ordinary phenol-aldehyde resin and hard rubber, on the other hand, are dark and are produced only in blacks, red-browns, and other dark colors.

There are two main coloring procedures: (1) surface coloring, performed on the artifact *after* forming by the application of surface coatings or coloring matters dissolved or dispersed in a suitable solvent; (2) all-through coloring, obtained by dispersing the coloring agents uniformly through the mix before or during forming.

The main coloring materials are organic dyestuffs and opaque inorganic pigments. Regardless of which are used, proper regard must be given to the following factors: (1) affinity for the binder and filler; (2) solubility and bleeding characteristics; (3) light-fastness; (4) heat stability; (5) chemical stability—resistance especially to the acidic, basic, or oxidizing catalyst that may be present.

Molding conditions, *i.e.*, temperature and time of heating, are also factors. The same coloring material in the same mix may yield different color values when molding conditions are changed.

Permanence must be considered as well as eye appeal. At times, one must be partly sacrificed to the other. As a rule, the inorganic pigments are less subject to change on prolonged exposure than the dyestuffs. Some general properties of coloring materials are presented in Table 8-4.

809. Surface-active Agents. In many industrial applications high polymers are employed as solid-liquid dispersions or liquid-liquid emulsions. The latter are often called latices. Examples are found among paints, adhesives, waterproofing materials, and fabric-modifying and finishing materials. To achieve satisfactory products of this sort it is often necessary to incorporate appropriate emulsifying agents, stabilizers, wetting agents, etc., which, as a group, constitute a highly important type of compounding ingredient.

Surface-active agents must be specifically chosen to meet the requirements of the particular system in which they are employed (Sec. 216).

This choice must be made with an eye both to their functional efficiency and to their effects on the finished product.

810. Other Compounding Ingredients. The compounding ingredients thus far discussed are those most frequently employed. However, many others are used for special purposes. Important examples are delustering agents applied to synthetic fibers, graphite incorporated into plastic bearings to make them self-lubricating, and the blowing agents added to create holes in cellular sponges and other expanded products (Sec. 853).

MOLDING, FORMING, AND MANIPULATION

811. Highly diverse techniques of molding, forming, and manipulation have had to be developed for producing the diversity of artifacts achieved by the high-polymer industries. In most instances analogous techniques are encountered in metallurgy and ceramics. Each technique is uniquely adapted to certain types of materials, but the fundamental variables that must be considered are always the same—temperature, pressure, and time. These in turn are governed mainly by the consistency and the behavior type of the mix, especially the binder (Sec. 323). Having considered the nature and functions of compounding ingredients, we are now ready to discuss the salient features of molding and forming techniques.

HOT COMPRESSION MOLDING

812. Distinguishing Features and Procedure. This molding method is commonly called simply *compression molding*. Its distinguishing features are the simultaneous application of heat and pressure to a fixed charge of mix in a closed mold.

The stationary and movable members of the mold are in position on heated platens between the top and bottom plates of a press (Fig. 8-1), usually with the mold cavity on the bottom platen and the mold plunger, or "mold force," attached to the top platen. Tie rods keep the press elements aligned, while guide pins serve the same purpose for the mold members during closing and opening of the mold.

The thoroughly mixed molding compound is placed in the mold cavity. An excess of about 5 per cent over that actually required to form the finished piece is usually added. This ensures a sharp impression and full pressure during molding. The press is then closed, forcing the movable member of the mold to compress the compound into the required shape. Under the combined action of heat and pressure, the binder soon fuses and exhibits plastic flow, and the compound takes the exact shape of the die. The excess material is squeezed out, forming a thin skirt of *flash*, which must be removed from the object during subsequent finishing

operations. If a thermosetting binder is being used, cross-linkage follows shortly after fusion and the material in the mold sets to form an object that is hard and rigid even at the elevated molding temperature. The mold is then opened, the finished piece is removed, a fresh charge is

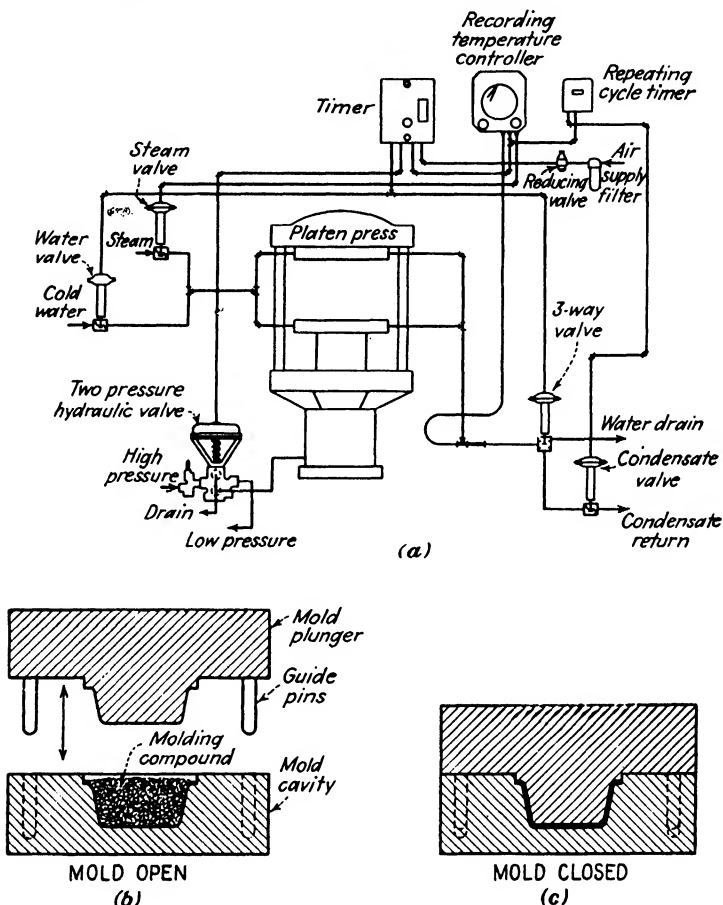


FIG. 8-1. Hot compression molding. (a) Control system for temperature, sequence, and duration of operations. [(a) Courtesy of Taylor Instrument Co. (b), (c) J. H. DuBois, "Plastics," American Technical Society, Chicago, 1945.]

introduced, and the entire cycle is repeated. Usually ejector, or knock-out, pins (not shown in Fig. 8-1) pass from the press plate through the wall of the mold to the inner mold surface. They push on the finished piece when the mold is opened and thus facilitate removal, which might otherwise be difficult.

813. Molding Cycles. When a thermosetting binder is used, the cycle consists of four steps as follows: (1) introduction of the charge;

(2) closing of the mold, during which full pressure is built up; (3) curing period, *i.e.*, successive fusion, flow, and hardening of the binder; (4) opening of the mold and ejection of the piece.

The time interval between the introduction of successive charges of molding compound is called the *cycle time*. To the molder it is of fundamental importance since it determines machine capacity and production schedules. Doubling the cycle time means halving the output while rent, labor, overhead, etc., remain essentially the same. The compression molding cycle time for thermosetting mixes ranges from 30 sec to several minutes, depending on molding conditions and the size and thickness of the piece.

When a thermoplastic binder is used in compression-molding equipment, the cycle takes much longer since two time-consuming steps must be added. After the curing period the mold must be cooled to a temperature below the softening point of the binder in order to allow the piece to harden sufficiently to permit opening of the mold. Then, after removal of the piece, the mold must be reheated to the proper molding temperature. Delmonte cites the following case: A telephone receiver, compression-molded from a phenol-aldehyde thermosetting mix, required a cycle time of 7 min. The same piece involved a compression-molding cycle of about 20 min when cellulose acetate, a typical thermoplastic, was used.

With some molding mixes, particularly those of the thermosetting type, a *breathing*, or *gassing*, *period* is highly desirable. After the mold has been closed, it is reopened for a short time to permit the escape of gases, such as entrapped air or steam or ammonia. Breathing may reduce the curing period, improve electrical properties, minimize after-shrinkage, or enhance quality and appearance by eliminating porosity, bubbles, or blisters. The correct duration and moment of introduction of the breathing period depend upon the particular operation and are best determined by trial.

814. Undercure and Overcure. Since high-polymer binders, as well as fillers and plasticizers, are mostly poor heat conductors with thermal conductivities 100 to 1,000 times less than those of metals, adequate heat transfer from the mold to the mix is always a problem. This problem grows more acute as the thickness of the piece increases. Both undercure and overcure are to be avoided, since each exerts detrimental effects. Undercured thermosetting molding material may exhibit any or all of the following shortcomings: mechanical weakness, poor solvent resistance, greater susceptibility to shrinkage and warpage after removal from the mold, flow marks, porosity, rough surface and impaired gloss, and impaired clarity (of transparent moldings) due to imperfect fusion and

entrapped gases. Overcuring, besides the obvious disadvantage of prolonging the molding cycle, may lead to heat discoloration, impaired mechanical strengths, and undulations on the surface. Sometimes the filler (notably cellulose) undergoes heat degradation. The effects of undercuring and overcuring upon the tensile strength of soft rubber vulcanizates are shown in Figs. 13-4, page 561, and 13-5, page 564.

815. Inserts. The utility of molded plastic artifacts is greatly enhanced by the technique of introducing metal, glass, or other inserts when and where needed. In complicated custom-molded jobs, as many as 20 or 30 metal inserts may be set in place and the plastic mix molded around them to produce the finished assembly. As may be readily understood, the introduction of inserts complicates mold design. Sufficient anchorage must be provided for the inserts and adequate provision must be made to hold them in place during the molding operation. This may be accomplished by introducing plain or threaded locating pins, recesses in the mold, or special clamping devices. During fusion and subsequent flow of a compression-molding mix, strong shearing forces are created, which tend to distort the inserts, move them out of the desired position, or even snap the locating pins. This is especially true if the inserts are at right angles or oblique rather than parallel to the direction of travel of the mold force.

816. Tableting and Preforming. A compression mold often has more than one mold cavity. Small objects such as bottle caps may be molded a gross at a time. The introduction of the correct weight of molding powder is difficult and messy, especially when the molding mix possesses a high *bulk factor*.

$$\begin{aligned}\text{Bulk factor} &= \frac{\text{apparent volume of loose molding mix}}{\text{volume of molded piece plus flash}} \\ &= \frac{\text{specific gravity after molding}}{\text{apparent specific gravity before molding}}\end{aligned}$$

The bulk factor is also known as the *compression ratio*.

To facilitate handling, the mix is often compressed in automatic machines into tablets, preforms, or blanks, each of which contains the correct weight of material and is of the correct dimensions and shape for the intended mold. Specifically, the advantages that may accrue from tableting and preforming are the following:

1. Since the bulk factor is reduced, the required depth of the mold cavity is also reduced. This means a lighter and less expensive mold.
2. The charge is handled more quickly, with greater cleanliness and often with less waste.

3. Heat transfer is improved because of the partial elimination of voids.

4. When preforms are used, the amount of flow required in different parts of the molding mix is made more uniform. Consequently, there is less tendency for flow marks to appear.

5. Inserts may sometimes be handled more easily by positioning them in a preform.

817. Preheating. Most molding mixes must normally be moisture-free before use anyway, so that it is often advantageous to preheat the molding mix prior to introducing it into the mold cavity, regardless of whether it is in powder, tablet, or preform condition. The material is brought to a temperature as close as feasible to the molding temperature. This may be done in an air oven or any other suitable device, preferably with the temperature and time of heating carefully controlled. With thermosetting mixes it is, of course, essential to control conditions in such a way that too much cross-linkage and premature hardening are avoided. For example, a phenol-aldehyde mix requiring a molding temperature of 350 F would be preheated to a temperature of about 210 F. The added cost of preheating may be more than compensated by the following advantages:

1. Shortening of the cycle time (as much as 50 per cent)

2. Less trouble with heat-transfer problems: (a) more uniform cure in thick sections; (b) flow commences earlier and is more uniform; (c) lower shearing forces set up during molding, hence less trouble with inserts

3. Improvement of product: (a) better electrical properties due to more complete removal of moisture; (b) less tendency toward porosity, blistering of surface, and flow marks; (c) less tendency toward internal stress in the finished piece

4. Lowering of mold maintenance costs: (a) less pressure required for closing mold; (b) less mold abrasion due to readier flow

818. After-baking. Very often, variations in material thickness make it impractical to cure a thermosetting molded article to its best mechanical strength in that full cure for the thicker sections may result in overcure of the thinner ones. Furthermore, it appears that thermoset molded articles, particularly the phenol-aldehydes, undergo dimensional shrinkage as well as an improvement in mechanical properties on aging at room or slightly elevated temperatures. Presumably this is attributable to a slow continuation of the polymerization reaction after molding.

Molded articles are subjected to after-baking for any or all of the following reasons: (1) to increase electrical resistivity; (2) to improve mechanical properties; (3) to ensure complete shrinkage before a molded part is put into use, especially where dimensional changes due to after-

shrinkage might cause operational difficulties; (4) to relieve internal stresses from a molded object. This annealing operation is particularly important in the case of glass.

The temperature and time of after-baking vary with the binder and the size and shape of the piece.

819. Hot-compression-molding Characteristics. The compression-molding characteristics of a few representative high polymers are shown in Table 8-5.

TABLE 8-5. HOT-COMPRESSSION-MOLDING CHARACTERISTICS

Material	Bulk factor*	Molding temperatures, deg F	Molding pressures, psi
Phenol-aldehyde.....	2-18	270-400	1,500-6,500
Melamine-aldehyde.....	2-15	275-370	1,000-6,000
Urea-aldehyde.....	2.2-3.0	280-330	1,500-6,000
Cellulose acetate.....	2.0-2.6	260-420	500-5,000
Cellulose acetate-butyrate.....	2.0-2.4	260-370	500-5,000
Ethylene.....	2.2-3.6	250-320	100-200
Ethyl cellulose.....	1.9-2.4	280-320	1,000-2,000
Methyl methacrylate.....	1.7-2.5	300-360	1,000-3,000
Styrene.....	2.0-2.3	275-375	1,000-10,000
Vinyl butyral.....	280-320	100-3,000
Vinyl chloride.....	~2	330-350	500-2,000
Vinyl chloride-acetate, rigid.....	~2	280-325	1,500-2,000
Vinyl formal.....	325-350	1,000-10,000
Vinylidene chloride.....	~2.0	220-350	500-5,000
Shellac.....	2-3	230-250	1,000-2,000
Hard-rubber-mineral filler.....	4-6	285-350	1,200-1,800
Tire-tread mix.....	~1.0	230-290	6-42

Data from several sources, mainly

PLASTIC MATERIALS MANUFACTURERS' ASSOCIATION, "Technical Data on Plastics," Washington, 1945.

* Also termed *compression ratio*. Tableting or preforming reduces these values to the range of 1.5 to 2.5.

Rubber goods are often vulcanized by what is essentially hot compression molding. The rubbery binder is broken down to a gumlike consistency by heat and mechanical working in a mill. Powdered compounding ingredients are then worked in to form a doughlike mass, which is then preformed and molded (vulcanized) by the simultaneous application of heat and pressure. Molding conditions for a tire-tread mix are included in Table 8-5.

INJECTION MOLDING

It was pointed out in the previous section that thermoplasts require considerably longer cycle times than heat-hardening materials when

compression molding is used. This increases production costs considerably. Injection molding was developed to enable the thermoplasts to compete successfully with the heat-setting compounds.

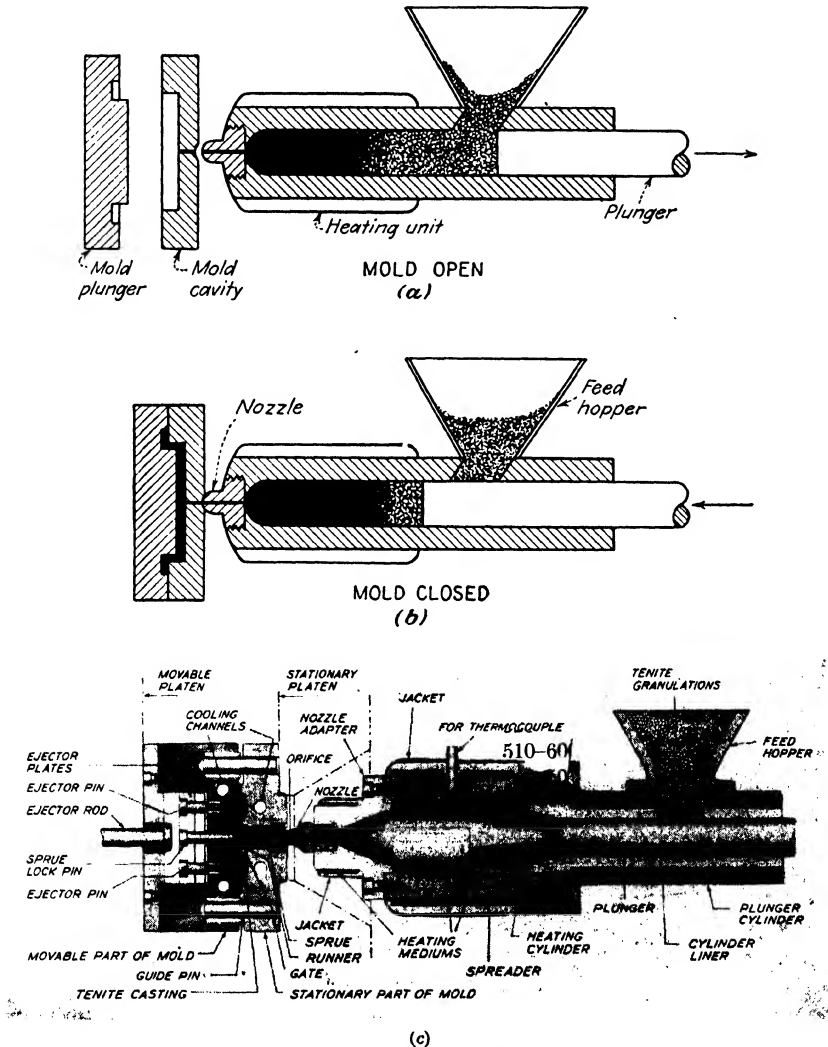


FIG. 8-2. Injection molding. [(a), (b) J. H. DuBois, "Plastics," American Technical Society, Chicago, 1945. (c) Courtesy of Tennessee Eastman Corp.]

820. Distinguishing Features and Procedure. Injection molding is characterized by the fact that the molding mix is preheated in a plasticizing cylinder to a temperature high enough for it to attain a quasi-liquid

condition and is then forced by a plunger through a nozzle into a closed mold which is cold enough to "freeze" the material to a solid sufficiently rigid for ejection. Molding mix in the form of granules, which have been thoroughly dried by oven heating, is fed into the plasticizing cylinder through a hopper (Fig. 8-2). When the mold opens, the cylinder plunger moves back, permitting material to drop into the cylinder. On the

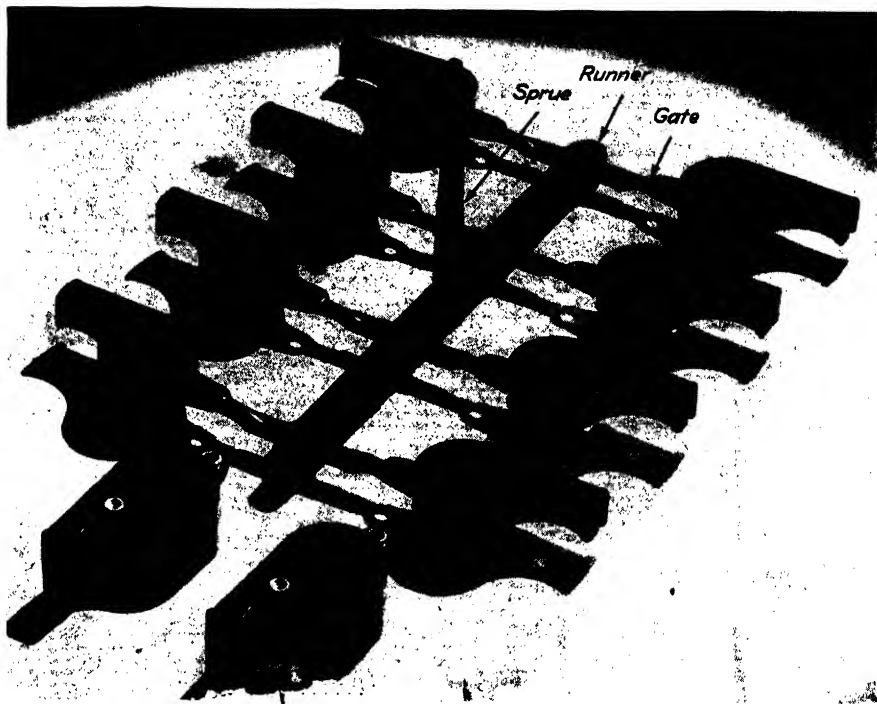


FIG. 8-3. Multiple cavity molding showing molded pieces, runners, and gates.
(Courtesy of Tennessee Valley Authority)

closing stroke the mold members lock tightly together, and the cylinder plunger moves forward, forcing the newly delivered material from the hopper into the heating zone of the cylinder. This material in turn displaces a "shot" of molten material through the nozzle into the mold cavity. The mold is cooled so that the shot hardens quickly. Conditions are controlled so that the molten plastic just has time to reach the outermost recesses of the mold cavity before flow ceases. When the mold is opened, the formed piece is loosened by knockout pins and removed, usually by hand. The function of the *torpedo* (also variously termed the *spreader* or *pineapple*) is to spread the mix into thin films and facilitate uniform heating as it passes toward the nozzle.

Most often a multiple-cavity mold is used, six or more pieces being

formed per shot. When the shot is removed, these pieces are all joined together (Fig. 8-3) by a network of material in the form of the sprue, runners, and gates. These latter are progressively thinner so that the individual pieces may be readily broken off at the gates. The sprue, runners, and gates represent scrap, which is ground up and returned into the process. Holding this scrap to 20 per cent or less is considered good.

821. Control of Conditions. The outstanding feature of injection molding is speed. Cycle times of 10 to 30 sec are common. Injection molding is more readily and generally applicable to thermoplastic than to thermosetting materials for the obvious reason that the latter tend to harden in the plasticizing cylinder. Furthermore, it is best suited for the molding of relatively small and relatively thin objects.

Injection molding requires a nice control over cylinder temperature, mold temperature, injection pressure, and time and rate of movement of material. The temperatures and pressures involved are both higher than those generally employed in hot compression molding. Injection-molding characteristics of different materials are found in Table 8-6.

TABLE 8-6. INJECTION-MOLDING CHARACTERISTICS

Material	Cylinder temperatures, deg F	Molding pressures, thousands of psi
Ethylene.....	325-375	4-30
Cellulose acetate.....	300-500	8-32
Cellulose acetate-butyrate.....	330-430	8-32
✓Ethyl cellulose.....	330-450	2-10
ΔMethyl methacrylate.....	325-480	10-30
Nylon.....	510-600	Low
Styrene.....	325-500	10-30
Vinyl butyral.....	250-340	15-30
Vinyl chloride.....	330-375	15-25
Vinyl chloride-acetate, nonrigid.....	280-330	7-30
Vinyl formal.....	350-400	10-30
Vinylidene chloride.....	300-400	10-30
Hard rubber.....	280-350	2-5

Data from several sources, mainly

PLASTIC MATERIALS MANUFACTURERS' ASSOCIATION, "Technical Data on Plastics," Washington, 1945.

Ejection temperatures usually lie between 100 and 200 F, depending upon the material.

The cylinder temperature is varied to suit the flow characteristics of the mix and the size of the mold cavity. Too low a cylinder temperature means insufficient flow, while too high a temperature or too long a period between shots may result in charring or decomposition or destruction of

coloring material. If the molding pressure is too low, flow marks tend to appear and definition may not be sharp. If it is too high, the finished piece may have high internal stresses and the impact strength may be poor. Finally, if the mold is kept at too low a temperature, freezing may take place in the runners, flow marks may appear, or the piece may lack mechanical strength. With too high a mold temperature the cycle is prolonged, and distortion may occur after ejection of the piece.

822. Advantages. Besides high-speed production, other advantages of injection molding over hot compression molding are low mold cost (since fewer cavities are needed for a given production rate), very low loss of material (since the scrap can be fed back into the process), and lower finishing cost (since there is no flash to get rid of).

823. Hardness Grades. The manufacturer of molding mixes will supply the molder with different colors and physical forms as needed, *i.e.*, powder, flake, granule, bead, etc. Each type of thermoplastic is also supplied in different grades suitable for compression, injection, extrusion, or other methods of molding. These grades are of different degrees of plasticity attained by the manufacturer through varying the amount and kind of external plasticizer, the degree of polymerization of the binder, and the symmetry of the binder molecules (by copolymerization or substitution). Thus the Tennessee Eastman Corporation sells cellulose acetate mixes under the trade name of Tenite I and cellulose acetate-butyrate mixes as Tenite II. Each is sold under various *types*; type A for injection, type C for compression. Each type in turn may be obtained in different *formulas*. For example, for Tenite I, formula 004 has particularly good molding qualities and extreme toughness but hardens relatively slowly in the mold, whereas formula 006 is exceptionally free-flowing and sets up quickly in the mold, effecting a short cycle time, but results in products of relatively low impact strength and extensibility. Finally, each type is supplied in various *hardness*, or *flow*, *grades*, which may range from H7 (hard, seventh degree) to S7 (soft, seventh degree). Table 8-7 is an example.

TRANSFER MOLDING

824. In the discussion of hot compression molding, attention was called to the fact that solid molding powder is fed into the mold and must pass successively through fusion, flow, and cure. It was also pointed out that during the initial stages of flow, when the plasticity of the material is low, tremendous shearing forces are set up which tend to distort or displace inserts and even snap off locating pins and, finally, that thick sections have a tendency to remain uncured in the interior, leading eventually to distortion and shrinkage of the piece after removal from the

TABLE 8-7. HARDNESS GRADES FOR TENITE II (CELLULOSE ACETATE-BUTYRATE) (FORMULA 201)

Property	Temperature, deg F.	Relative humidity, %	H5	H4	H3	H2	H	MH	M	MS	S	S2	S3	S4	S5
Flow temperature, deg F.	341	332	323	314	307	300	293	286	279	272	266	260	254
Specific gravity.....	77	50	1.20	1.20	1.20	1.19	1.19	1.19	1.18	1.17	1.17	1.16	1.16	1.15	1.15
Hardness, Rockwell M scale.....	77	50	68	67	66	64	63	61	58	55	50	43	35	30	23
Elongation, % 2 in. gauge.....	77	50	39	45	46	50	53	55	58	61	64	67	70	73	76
Isod impact strength, ft-lb/in. molded notch.....	-40	..	0.4	0.5	0.5	0.6	0.6	0.6	0.7	0.8	0.9	1.1	1.3	1.5	1.7
	77	50	0.8	1.0	1.2	1.5	1.7	1.9	2.2	2.5	2.9	3.4	4.0	4.6	5.2
Tensile strength, psi.....	-40	..	9,500	9,400	9,400	9,300	9,200	9,100	8,900	8,600	7,900	7,100	6,500	5,900	5,300
	77	50	6,300	6,100	5,800	5,500	5,200	5,000	4,700	4,300	4,000	3,500	3,000	2,700	2,300
Tensile upper yield point, psi.....	160	..	4,600	4,200	3,800	3,500	3,100	2,700	2,400	2,100	1,700	1,300	1,100	800	600
	77	50	6,000	5,800	5,500	5,200	4,900	4,700	4,400	4,000	3,500	3,000	2,500	2,100	1,700
Tensile lower yield point, psi.....	160	..	3,800	3,500	3,300	3,000	2,600	2,400	2,100	1,800	1,500	1,200	1,000	600	300
	77	50	5,300	5,100	4,900	4,600	4,400	4,100	3,900	3,500	3,200	2,700	2,300	1,900	1,500
Flexural strength, psi.....	160	..	3,100	2,900	2,600	2,300	2,000	1,900	1,700	1,500	1,200	1,000	700	500	200
	-40	..	16,100	15,800	15,400	14,900	14,500	14,200	13,700	13,200	12,000	10,200	8,700	7,300	6,100
	77	50	10,000	9,500	9,000	8,500	8,100	7,600	7,000	6,300	5,400	4,400	3,600	2,800	2,100
Modulus of elasticity, psi $\times 10^{-6}$	160	..	6,400	5,600	5,100	4,300	3,800	3,200	2,700	2,200	1,500	1,100	800	500	400
	-40	..	2.03	1.99	1.95	1.90	1.86	1.81	1.75	1.67	1.53	1.36	1.21	1.08	1.00
	77	50	1.73	1.69	1.65	1.60	1.56	1.50	1.43	1.33	1.18	1.03	0.90	0.80	0.70
Water absorption (24-hr. immersion), wt gain, %.....	160	..	1.18	1.17	1.14	1.11	1.07	1.03	0.97	0.85	0.69	0.50	0.33	0.24	0.16
	77	..	2.0	1.9	1.8	1.7	1.6	1.5	1.5	1.4	1.4	1.4	1.3	1.3	1.2
Soluble matter lost, %.....	77	..	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Accelerated aging (1 week), wt lost, %.....	150	..	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Shrinkage, %.....	150	..	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Distortion under heat, deg F.....	178	166	155	146	140	134	129	124	120	116	113	110	106
Deformation under load (cold flow), %.....	122	..	2.4	3.8	6.0	9.7	13.8	19.6	27.3	33.6	37.4	40.3	42.5	44.6	46.6

Courtesy of Tennessee Eastman Corp.

Formula 201 is the most widely used of all Tenite formulas, for extrusion as well as injection. It has the highest impact strength both at ordinary and at low temperatures, for this reason being selected for applications requiring maximum serviceability over a wide temperature range. Flows of H and H2 are used for extrusion; MS is ordinarily used for injection and compression. Applications: screw-driver handles, toothbrush handles, razor boxes; continuous extrusion—refrigerator drain tubes, airplane fuel lines, tooth-powder containers.

mold. Transfer molding was invented to overcome these difficulties. It is in many respects an injection-molding technique applied to thermosetting materials.

825. Distinguishing Features and Procedure. Transfer molding is the process whereby a thermosetting mix is subjected to sufficient heat and pressure in a "plasticizing pot" or "loading well" to convert the mix

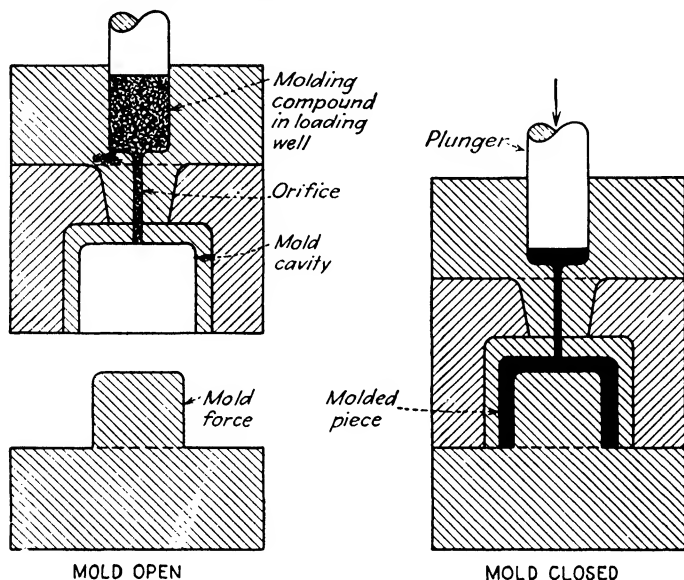


FIG. 8-4. Transfer molding. (J. H. DuBois, "Plastics," American Technical Society, Chicago, 1945.)

to a quasi liquid, after which it is forced by a plunger into a closed mold kept at a temperature high enough to cause rapid heat hardening to take place. In other words, it is similar to the injection molding of thermoplasts in many respects but differs from it in that the injection-molded thermoplasts are "frozen" to a rigid condition in a relatively cold mold, whereas the transfer-molded thermosets are heat-hardened to the rigid state in a relatively hot mold,

Figure 8-4a shows the overhead transfer pot and the mold both in position between the platens of a press. The mold is closed and still empty except for inserts, ready to receive the shot of heat-plasticized mix from the transfer pot through the properly designed orifice. Figure 8-4b shows the mold still closed after receiving the shot. The mold is not opened until the shot has heat-hardened.

826. Materials for Transfer Molding. Since the material being heated in the plasticizing pot contains functional linear polymers, it is obvious that temperature and time of heating must be so controlled that

the mix does not set up in the pot and jam the machine. Since heat hardening is a chemical reaction, it is dependent upon temperature. The plasticizing-pot temperature is kept at a point where the binder will fuse without hardening rapidly. For example, the setting time of a wood-flour-filled phenol-aldehyde molding mix may vary as follows:

Temperature, deg F	Time Required to Heat-harden, sec
356	34
302	68
267	170

In preparing superior transfer-molding binders, recourse may be had to keep the degree of cross-linkage originally low and incorporating less active catalyst or even inhibitor.

Although the transfer-molding technique has been successfully applied to all the commercial types of thermosetting materials, including vulcanizable rubbers, some are better adapted to the purpose than others. The urea-aldehydes are somewhat critical, in that the setting time is strongly dependent on temperature within a relatively narrow range. The melamine-aldehydes, on the other hand, set more slowly. Because of their longer flow period they are every bit as adaptable to the method as the phenol-formaldehydes. Perhaps best of all are the phenol-furfural resins, whose setting time is longer at low temperatures and yet shorter at curing temperatures than those of the phenol-formaldehydes (Sec. 1614). It has been found possible to prepare phenol-furfural resins that may be held for 45 min at a temperature sufficiently high to cause fusion and yet not heat-harden. They may be not only transfer molded but even injection-molded continuously. Blends of phenol-formaldehyde and phenol-furfural resins have been found particularly suited for making transfer-molded articles of highly desirable properties.

Although identical in principle, the transfer molding of vulcanizable rubbers requires somewhat different machinery owing to the radically different rheological properties.

827. Advantages. The advantages of transfer molding are as follows:

1. Since the mix flows into the mold cavity in a highly heat-plasticized condition, there are no high initial unbalanced pressures. Very delicate inserts may be handled without distortion or displacement. Fine wire and glass inserts may be used. Long fine holes, only a few thousandths of an inch in diameter, are made possible. Inserts may run along any desired axis. Intricate shapes, not attainable by compression molding, are readily produced. Flow marks are eliminated.

- 2 Thick pieces cure with almost complete uniformity since the mix

enters the mold hot and the problem of heat transfer is minimized. Cycle times are often shortened.

3. Owing to uniform and thorough cure throughout, shrinkage and distortion are at a minimum so that close dimensional tolerances may be met.

4. For the same reason, the mechanical strength and the density of the piece are greater.

5. Since the mold is fully closed before the shot is received, flash or fins are entirely eliminated, resulting in lower finishing costs. This is particularly important where fibrous or shredded fabric fillers are used. When such mixes are compression molded, there is normally a heavy, tough flash, which must be cut off with a knife, a costly operation.

6. Air and other occluded gases are expelled in the plasticizing chamber so that blistering is practically eliminated.

7. Mold costs are reduced. Molds do not have to be so elaborate, and abrasive action is greatly reduced.

EXTRUSION

Extrusion is a molding process aptly compared with the squeezing of tooth paste from a tooth-paste tube. It is the most efficient and most rapid method of producing long, continuous members such as tubing, rod, and filament. In one modification or another it is used in many high-polymer industries.

828. Distinguishing Features and Procedure. The process consists in forming the mix into a long, continuous member by forcing it under pressure through the orifice of a die, the cross section of the member being identical with that of the orifice. Tubes, rods, filaments, angles, channels, and sheets as well as members of more complicated cross section are producible via extrusion.

In all extrusion it is essential that the mix be in a highly plastic condition at the moment it is forced through the die. This plasticity may be attained by heat or by the incorporation of large amounts of external plasticizer or even of volatile solvent. When a dry flake, granule, powder, or dough is fed into the equipment, the process is differentiated as *dry* extrusion. If, on the other hand, the feed contains volatile solvent in appreciable quantity, the process is known as *wet* extrusion.

The equipment used for dry extrusion somewhat resembles that employed for injection molding. The essential features (Fig. 8-5) are a feed hopper leading into a plasticizing cylinder usually fitted with a screw conveyer, which forces the mix toward the die at a uniform rate and pressure. As the mix moves forward, it is heated to progressively higher temperatures so that it emerges from the orifice in a highly plastic

condition. A torpedo is often employed, as in injection molding. Upon emergence from the die the extruded member is laid down continuously in a groove in a moving conveyer belt and immediately subjected to a cooling blast of air so that the material will harden sufficiently to maintain its dimensions and shape within reasonable limits. Sometimes the conveyer belt is made to travel faster than the rate of extrusion so that tubing or rod may be drawn to smaller diameters. In making tubing, provision is often made to blow a continuous blast of air through the *inside* to prevent it from collapsing.

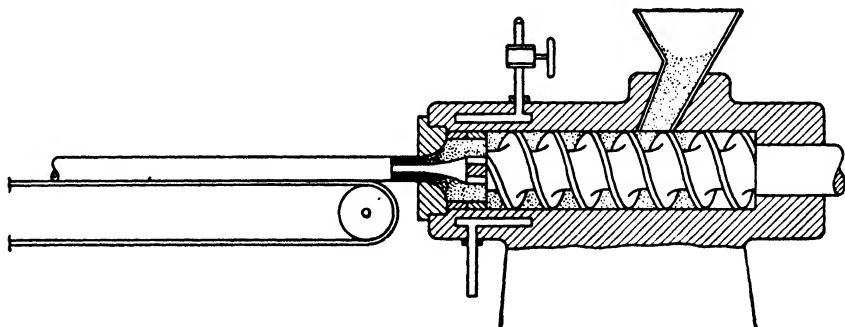


FIG. 8-5. Type of extrusion machine used for extruding acetate tubing. (H. R. Simonds and C. Ellis, "Handbook of Plastics," D. Van Nostrand Company, Inc., New York, 1943.)

When wet extrusion is employed, the solvent must always be evaporated from the member under carefully controlled conditions.

Electrical wire is often coated with insulation by extruding the insulation on the wire as it passes continuously through the die.

829. Materials for Extrusion. Practically any thermoplastic material may be extruded. Commercially prominent examples are rubber, cellulose acetate, cellulose acetate-butyrate, ethyl cellulose, polystyrene, polymethyl methacrylate, polyvinyl chloride, polyvinyl chloride-acetate, and polyvinylidene chloride. Cellulose nitrate is wet-extruded since it has a tendency to decompose and cause fires or explosions if handled dry. Each material requires its own special modifications of the extrusion equipment as well as its own conditions.

SPINNING OF SYNTHETIC FIBERS

830. The spinning of all synthetic fibers involves what is essentially an extrusion process. However, fiber spinning is different enough to merit separate discussion.

There are three commercial methods for spinning synthetic fibers, all of which involve two fundamental operations, (1) extrusion of monofilaments and (2) the elongation of these original filaments under tension. The object of the latter step is to orient the linear-polymeric molecules

along the fiber axis and hence increase the intermolecular forces of attraction. As previously mentioned, increases of 300 per cent or more in the tenacity accompany the drawing process. (For discussion of tenacity see Sec. 1108.) A continuous yarn or thread of a desired weight may be made by twisting together either a large number of fine filaments or a smaller number of coarser filaments. The former will be more expensive but stronger and more pliable.

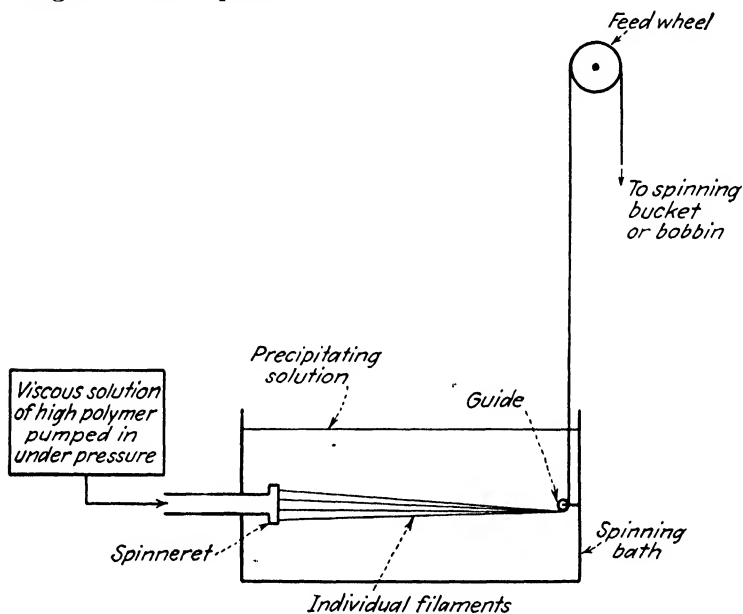


FIG. 8-6. Wet spinning.

831. Wet Spinning. In wet spinning (Fig. 8-6) a viscous solution of high polymer is made by dissolving the latter in the correct amount of an appropriate solvent. After it has been rigorously freed of air and carefully filtered, this solution is then pumped under pressure through the fine holes of a spinneret into a spinning bath containing a reagent that reacts with the soluble polymer and precipitates it instantly in the form of continuous filaments of insoluble material. The spinneret may have any desired number of holes. These holes may be coarse or fine and of different cross-sectional shapes, depending upon what type and weight of filament are desired. The individual filaments are brought together by passing under a guide rod or pulley and are then passed over a feed wheel. From there they go to a spinning bucket.

By one means or another, tension is applied to the freshly formed filaments, which undergo considerable elongation accompanied by molecular orientation along the axis of drawing. Continuous-filament yarn

is made by twisting a number of filaments together. *Staple fiber* is produced by chopping the filaments to any desired *staple length*.

During drawing, the filaments usually acquire a luster, often greater than that of silk. For many textiles this is undesirable, and the filaments are delustered under controlled conditions. One method is to add oils, waxes, or the like, to the spinning bath, where they are taken up by the fibers. Another method is to disperse extremely finely divided titanium oxide in the high-polymer solution itself. The particle size must be such

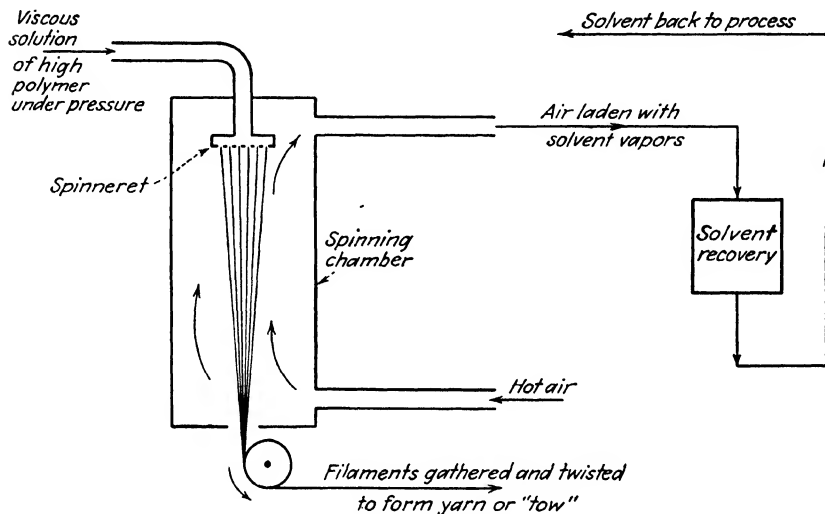


Fig. 8-7. Dry spinning.

that this material is not removed during filtration and does not clog the holes of the spinneret. The fundamental requirement for a delustering agent is that it have a refractive index different from that of the fiber polymer. This results in scattering of light and breaks up the continuous specular reflection from the fibers (Secs. 1017 and 1018).

From what has gone before it is evident that the synthetic-fiber manufacturer can turn out fibers of almost any desired diameter, length, and luster. Even the shape of the cross section can be controlled.

Viscose rayon, cuprammonium rayon, rubber, and casein fibers are commercial examples of wet-spun materials.

832. Dry Spinning. In dry spinning (Fig. 8-7) a viscous solution of the fiber polymer in a suitable solvent is pumped under pressure through the spinneret into a chamber through which a current of hot gas is passing. The solvent evaporates, leaving behind continuous coagulated filaments of the polymer. The filaments are subjected to tension, being drawn out of the spinning chamber at a faster rate than they are being extruded into

it. The filaments are gathered over a pulley as they leave the chamber and are twisted together to form a yarn, or *tow*. The solvent is recovered and returned to the process. Cellulose acetate rayon and polyvinyl chloride-acetate are dry-spun commercially.

It is important to note that, unlike wet spinning, no chemical modification of the fiber polymer takes place. In wet spinning the fiber is formed by precipitation or regeneration of the fiber polymer. In dry spinning the fiber formation involves merely evaporation of a solvent.

833. Melt Spinning. The third commercial spinning method is called *melt spinning* and is characterized by the fact that no solvent is added to the fiber polymer. Suitable plasticity is attained by heating the latter *per se* to a temperature above its melting point. The resulting melt is extruded in the form of relatively coarse monofilaments, which are then drawn to several times their original length. The usual changes accompany elongation, *viz.*, the tensile strength, pliability, melting point, and luster increase, the solubility decreases, and so on.

Nylon, polyvinylidene-vinyl chloride (*e.g.*, saran), and Fiberglas are commercially important examples of melt-spun fibers. Some of these may be cold-drawn, *i.e.*, elongated under temperatures well below the melting point.

HIGH-FREQUENCY, OR DIELECTRIC, HEATING

834. This method of heating is also unfortunately termed *electronic heating*. In all the hot-forming methods thus far described, as well as in others such as plywood manufacture, there have been, in the past, serious limitations upon the size and thickness of articles that could be successfully molded. With conventional heating methods there is always the serious problem of heat transfer to the interior of the mass, since polymeric binders and fillers are thermal insulators. Hence, the exteriors of thick sections are scorched before the interiors are cured.

This difficulty has been minimized by the introduction of dielectric heating. The nonconducting material to be heated is placed between metal electrodes and is made the dielectric of a capacitor. The electrodes are then connected to a high-frequency generator. The applied voltage causes an orientation of the molecular dipoles (both permanent and induced), and the high-frequency alternation produces corresponding changes in orientation many times a second (Sec. 1008). The work required to effect these molecular reorientations is transformed into heat. In a very short time the material is hot, and, what is more important, *the heating is uniform*, since the molecules in the interior of the mass undergo exactly the same process as those on the surface. Dielectric heating thus makes possible sizes and thicknesses that would previously have been

considered fantastic. Moldings of bathtub or office-desk proportions are entirely feasible. Other advantages that may be cited are the following.

1. *Saving of time.* In compression molding, mold-closing times have been cut from 90 sec to 15 or 20 sec. A thick preform may be uniformly preheated to 275 F in a matter of 30 to 40 sec (Fig. 8-8). In the production of one particular phenolic molding 2 in. thick, the sum of preheating, mold closing, and curing times was 22 min by conventional methods against 2 min and 50 sec with dielectric heating. Transfer-molding-cycle times have been reduced 300 per cent or more. Plywood gluing has in some instances been cut from 4½ hr to under 5 min (Fig. 8-9a).

2. *Improvement of product.* Stratification, *i.e.*, weak uncured regions in the center of a (thick) piece, is eliminated. The finished article is relatively free of internal stresses. Hence warpage and shrinkage are reduced.

3. *Saving in equipment costs.* Since the mix may be preheated in such a short time that scorching and presetting are avoided, the mix may enter the mold in a far more plastic condition. As a consequence, molds may be lighter, and smaller presses may be used.

4. *Better control over heating.* Power and hence heating can be shut off instantaneously. By the use of a radio-frequency "gun," or "stapler," heat may be applied at one point or along one seam. Spot gluing and welding are thus possible (Fig. 8-9b).



Fig. 8-8. Preform preheating by high frequency. A preform is shown being placed into position for preheating. In order to protect operator current cannot go on until safety cage is closed. (Courtesy of RCA Victor Div., Radio Corp. of America.)

JET MOLDING

835. Distinguishing Features and Procedure. Jet molding is a natural outgrowth and extension of transfer molding. In essence, it is a method of continuous injection molding that is applicable to thermosetting as well as thermoplastic mixes. The distinguishing feature of this molding technique is that the molding mix is heat-plasticized by

applying intense heat instantaneously as the shot is forced under pressure from a cylinder through a fine nozzle into a closed mold. The intense heat is applied only as the shot passes through the steel nozzle, which is induction-heated (Fig. 8-10). In other words, jet molding is really the

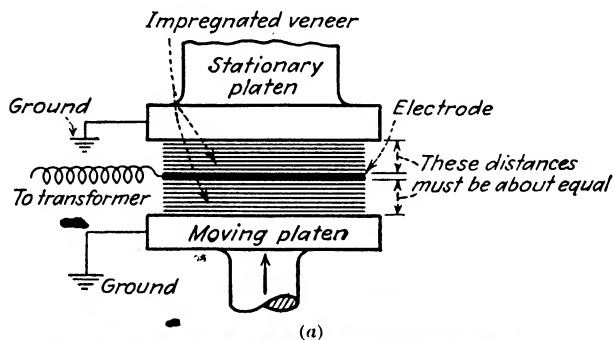


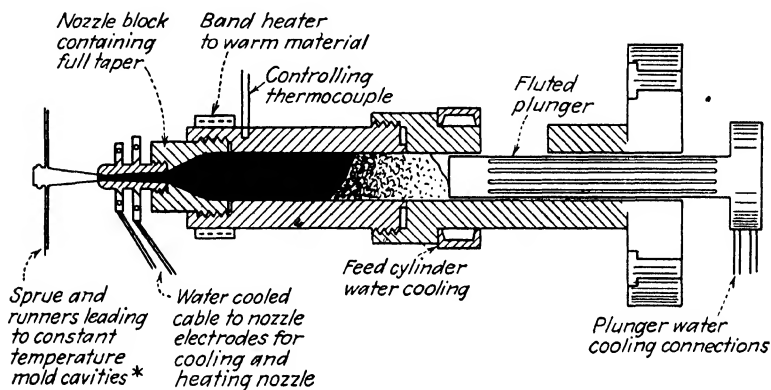
FIG. 8-9. Applications of dielectric heating. (a) Press setup for dielectric heating of laminates. (*J. Sasso, "Plastics Handbook for Product Engineers," McGraw-Hill Book Company, Inc., New York 1946.*) (b) High frequency "gun" being used to spot-glue assembly. (*Courtesy of Steinway and Sons and Modern Plastics Encyclopedia, New York.*)

application of a new heating technique rather than a new method of molding.

The mix is fed into a hopper and from thence falls into a feed cylinder, very much as in injection molding. The material is then moved forward toward the nozzle end of the cylinder by pressure applied by the injection plunger. Pressures range from 15,000 to 90,000 psi, depending upon the character of the mix. As the mix nears the nozzle, mild heat is applied. Temperatures of 150 to 200 F are maintained, *i.e.*, the mix is merely

warmed in this zone, but under the high pressure of the injection plunger it is forced to begin to flow into the nozzle. No torpedo, or spreader, is used.

Placed around the nozzle are two or more electrodes by means of which intense heat is generated by induction. This heat is transferred to the thin stream of mix as it passes through the nozzle. By this means the temperature of the mix is raised almost instantaneously to 400 to 1200 F, depending on the nature of the binder, the nature and amount of filler, and the size and complexity of the mold. This temperature is far



FEATURES OF JET MOLDING HEATER

* Jet molds are heated to restore heat lost by conduction etc., since molding heat is substantially all added in nozzle

Fig. 8-10 Sectional view of jet-molding unit. (Courtesy of *Modern Plastics Encyclopedia*, New York.)

in excess of that which the mix could withstand over any appreciable time interval.

As soon as the molten shot has passed through the nozzle and enters the mold, it is subjected to cooling and hardens either by cross-linkage or by freezing, depending on whether it is thermosetting or thermoplastic. After the injection of the shot is complete and the mold is filled, the injection pressure is released, the induction heating is shut off, and the nozzle itself is cooled rapidly by water, which is kept circulating continuously through the electrodes. This is necessary (1) to prevent the material left in the nozzle from undergoing thermal decomposition or cross-linkage and (2) to prevent the transfer of heat to the mold or cylinder. At the start of the next cycle, the heat and pressure are again applied.

Jet molding is sometimes called the *hot-cold nozzle process*.

836. Applicability and Advantages. As may be readily understood, jet molding requires precise control over temperature, pressure, and heating time, as well as synchronization of nozzle heating with injection-plunger travel. Incorporation of the proper lubricant into the molding mix is likewise of prime importance. Zinc stearate has been found to be effective in many cases. Jet molding is applicable with excellent results to both thermoplasts and mutaplasts. All types of thermosetting resins, thermoplastic resins, and natural and synthetic rubbers have been successfully handled.

Among the advantages of jet molding are high speed and the product improvements that are the natural concomitants of uniform, thorough cure, *viz.*, uniform dielectric properties, greater dimensional stability, and less porosity.

Strangely enough, another outstanding advantage is the ability to mold heat-sensitive mixes. The interesting fact is that many high polymers subjected to intense heat for a few seconds undergo far less pyrolysis than they do when heated to lower temperatures for longer time intervals. Both jet molding and dielectric heating have resulted in major improvements in both the plastics and rubber industries.

CASTING

837. Distinguishing Feature. The distinguishing feature of casting is that the mix is poured in liquid condition into an open mold, where it sets to shape without the application of pressure.

838. Usual Procedure. One might think offhand that almost any commercial thermoplastic binder could be softened by heat alone to a point where it would be sufficiently fluid to be poured into open molds and allowed to set to shape. Quite to the contrary, most of them reach a decomposition temperature before they are sufficiently fluid for such handling. Nor does the answer lie in the simple expedient of adding external plasticizer since, in most cases, if enough of the latter is added to permit of casting, the resulting product is lacking in mechanical strength. Addition of volatile solvent is also ineffective, for so much shrinkage occurs that definition is destroyed.

The more usual procedure is to polymerize the binder to a low degree of polymerization where it still has a sirupy consistency. Catalyst, pigment, dye, etc., are incorporated, and this liquid mix is then poured into the mold, where it polymerizes to a solid condition under the influence of heat, usually at relatively low temperatures.

Mold costs are low. Rubber, lead, wood, glass, and plaster of paris molds are used, depending on the plastic and the nature of the finished product.

839. Materials for Casting. By this method, acrylic resins are cast into stock-size rods and sheets of exceptional clarity. Polystyrene has been similarly formed into radio parts, although difficulties arise from the pronounced dimensional shrinkage during polymerization.

The most important cast plastics are the phenol-aldehydes. Poured into open molds in the form of specially prepared liquid resin (Sec. 1610), they are caused to space-polymerize. The resulting products are

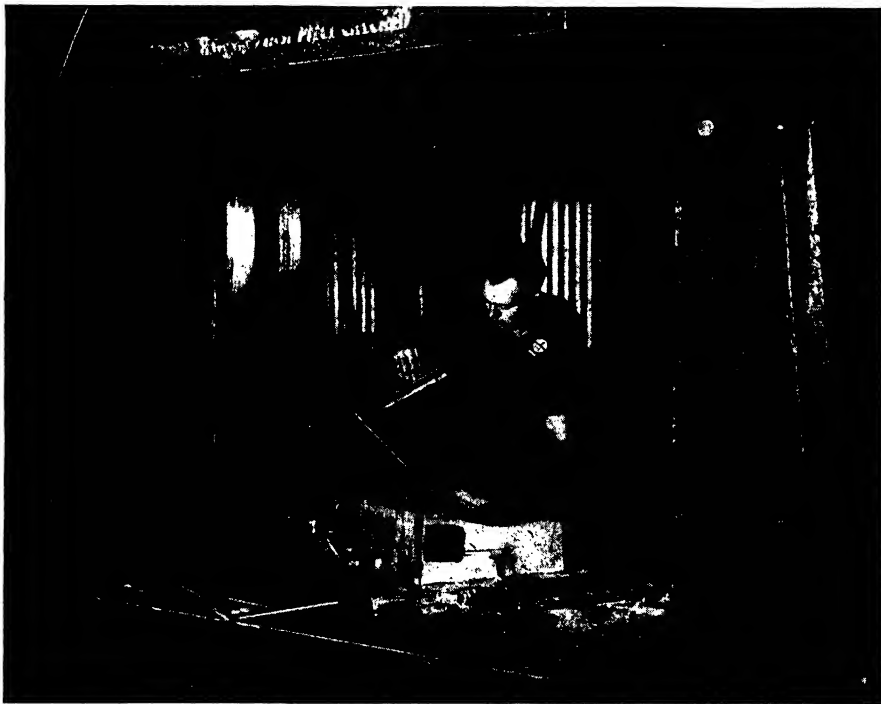


FIG. 8-11. Drop hammer comprised of a cast thermoplast punch and die for forming aluminum sheet parts. (Courtesy of Lockheed Aircraft Corp.)

characterized by relative freedom from internal stress and excellent machinability.

The temperatures employed in the hot molding of ordinary phenol-aldehydes range from 270 to 360 F. The resulting resins are deep red or red-brown owing to the formation of quinoid color bodies. However, by starting with specially purified phenol and formaldehyde and manufacturing liquid casting resin in special nickel or stainless-steel equipment and, finally, by space polymerizing in the casting molds at temperatures of 158 to 176 F for 3 to 8 days, it is possible to avoid the formation of color bodies and produce resins that are almost water-white. By the

incorporation of suitable dyes and pigments, exceptionally beautiful materials can be made. Since the cast phenolics are also outstandingly hard and take a high polish, these materials are used for making artificial gems, objects of art, and decorative fixtures. They can be very successfully machined, cut, carved, or otherwise fabricated. For obvious reasons, they are expensive.

840. Permanently Castable Plastics. Ethyl cellulose has been developed commercially into permanently castable plastic. The polymer is plasticized with one or another suitable external plasticizer to yield products that may be liquefied by heat alone (~ 400 F) and poured into open molds to set. When cold, the material is hard enough and tough enough to be used for drop-hammer and hydraulic-press punches but can nevertheless be heated, reliquefied, and recast. Similar products may be obtained from cellulose acetate-butyrate.

Much lighter than lead and far tougher, the plastic punches outlast and outperform those previously used and have contributed heavily toward speeding the production of parts made of light metals (Fig. 8-11).

COLD MOLDING

841. Cold molding is different from other molding methods in that the mix is first squeezed to shape by the action of pressure alone in a cold mold and then baked in an oven to set the binder. In other words, pressure and heat are applied separately. It is not until after the piece has been baked and the binder has set that the article has any appreciable mechanical strength.

Production is rapid since the molding-cycle time is usually around 10 sec and many pieces may be baked simultaneously. The cold-molding technique is encountered in the ceramics industry and in powder metallurgy as well as in the plastics field.

Three types of binders are commonly used: cement, bitumens, and phenol-aldehydes. Filler percentages run high, often of the order of 80 per cent. Asbestos is very commonly used. Molding pressures of 4,000 to 12,000 psi are common, and in some cases pressures of several hundred thousand pounds are employed. Mold wear is severe. For obvious reasons, the finished articles lack the surface smoothness, gloss, and appearance that characterize hot-molded pieces. Furthermore, dimensional differences are relatively large.

The baking operation requires 1 to several days. When organic binder is used, the baking starts at about 200 F and the temperature is raised slowly to avoid blistering and warping, finally attaining about 450 F. With inorganic refractory binders much higher baking temperatures are encountered.

Cold molding is valuable for the manufacture of electrical insulating fixtures since the finished pieces exhibit high arc resistance and heat resistance. Properties of cold-molded materials made with the three types of binders are found in Table 8-8.

TABLE 8-8. PROPERTIES OF COLD-MOLDED MATERIALS

Type of binder	Bitumen*	Phenolic resin	Portland cement
Tensile strength.....	700 to 1,000 psi	2,000 to 2,500 psi	1,200 to 1,500 psi
Compressive strength.....	3,000 to 4,000 psi	12,000 to 13,000 psi	15,000 to 18,000 psi
Modulus of rupture.....	1,200 to 1,500 psi	4,000 to 6,000 psi	4,500 to 5,500 psi
Impact (Izod).....	0.5 to 1	1 to 2.5	2 to 4
Rockwell hardness 14-in. ball, 100 kg load, B scale.....	10 to 20	40 to 50	60 to 80
Dielectric strength.....	50 to 100 volts/mil	100 volts/mil	75 to 100 volts/mil
Water absorption in 48 hr.....	1 to 3%	$\frac{1}{2}$ to 1%	3 to 12%
Specific gravity.....	1.9 to 2	2 to 2.5	2 to 2.5
Standard color.....	Black to brown	Brownish yellow to black	Light gray to black
Distortion under heat.....	Slight after 400 F	None up to 300 F	None up to 1,000 F
Heat resistance before change.....	600 F	400 F	1500 F
Chemical resistance.....	Resistant to all acids and alkalis unless concentrated and above 70 F		
Arc resistance.....	Good	Low	High

BOONTON MOLDING COMPANY, "A Ready Reference for Plastics," Boonton, N.J., 1943.

* Bitumen binders consist of asphalt or gilsonite, drying oil, and, occasionally, small percentages of natural gums.

BLOWING

842. Blowing is a molding technique particularly useful for making hollow objects. It is one of the oldest of molding methods, having been used for making glass bottles and globes centuries ago. Essentially it consists in forcing a layer of plastic mix against the walls of a mold cavity by the internally applied pressure of air or steam and holding it there until it has taken the desired hollow shape. The gas under pressure is introduced through an inserted blowpipe, and the mold consists of matching halves, which are usually hinged to one another to facilitate closure and removal.

There are many modifications to the main procedure, depending on the nature of the mix being handled. Glass is blown by taking up a molten blob on the end of the blowpipe, inserting the blob into the open mold, closing the mold, expanding the blob by blowing air under pressure into the pipe, and finally opening the mold and removing the piece after it has frozen to shape against the cold walls of the mold.

In the blowing of organic thermoplasts, the mix is often handled in the form of highly plasticized, flexible sheets. Two such sheets are introduced between the mold halves and project beyond the mold cavity so that when the mold is closed they are pinched against one another all

around the periphery. Air or steam is introduced between the sheets through the blowpipe, forcing them against the walls of the hot mold. Meantime, the edges of the sheets are fused together by the combined action of heat and pressure. The mold is then cooled till the piece is sufficiently rigid for removal (Fig. 8-12). There is, of course, always a skirt of "flash" along the parting line of the mold where the sheets have been pinched together. This must be removed.

Hollow, collapsible items such as hot-water bottles, football bladders, and atomizer bulbs are often made from rubber by the above

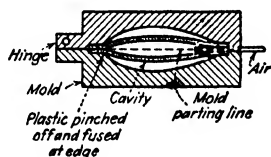


FIG. 8-12. Blowing hollow article from sheet stock. (J. H. DuBois, "Plastics," American Technical Society, Chicago, 1945.)

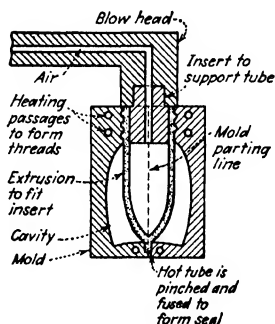


FIG. 8-13. Blowing hollow article from tubing stock. (J. H. DuBois, "Plastics," American Technical Society, Chicago, 1945.)

technique. Steam is used as the pressure gas, and the mix is vulcanized (cross-linked) during the process.

Instead of using sheets, one may introduce the stock into the mold as a preformed, extruded tube. One end of the tube is pinched shut between the mold members. From then on, the procedure is similar to that already described. Figure 8-13 shows the setup for blowing an "unbreakable" plastic bottle from an extruded tube preform.

Celluloid (cellulose nitrate) and rubber have been blown for years. There is no inherent reason why any thermoplastic cannot be blown. In modern bottlemaking machines, glass blowing is conducted on a grand scale as a continuous process. Considerable attention is being devoted to the possibilities of combining extrusion or injection molding with blowing to put the manufacture of hollow plastic articles on a similarly continuous, completely automatic basis.

EMULSION PROCESSING AND MANIPULATION

843. Owing to their great length, when high-polymer molecules are dissolved in a true solvent, the viscosity often attains inordinately high values even when the solute content is no more than a few per cent. If such a solution is used for building up a coating, impregnating a solid, or forming a glue joint, an inadequate amount of polymer substance may

remain after the solvent has evaporated. Multiple-step processing, which is costly and time-consuming, may be necessary. Furthermore, adequate impregnation of a substrate may be impossible. By contrast, the dispersed particles of a high-polymer emulsion are comparatively large and essentially spherical. The viscosity may be due mainly to the hydrodynamic effect and is often one or more orders of magnitude lower than that of a true solution of equal concentration. The processing and manipulation of emulsions, notably aqueous dispersions, are therefore often highly advantageous. The amount of polymer substance laid down in one application may be greatly increased, and in cases where proper impregnation is impossible with a true solution it may be adequate with the emulsion. Also, in the case of aqueous emulsions water is used in place of solvents which are expensive and may be objectionable on the grounds of toxicity, odor, or fire hazard.

Many synthetic rubber and plastic polymers are produced as emulsions, or *latices*, by the emulsion-polymerization technique (Sec. 425). If the latex may be used directly, instead of first isolating the polymer in bulk and later dissolving or otherwise redispersing it during manipulation, obvious economic advantages accrue.

Emulsification implies the presence of a dispersing phase considerably different in polarity, chemical constitution, and solubility from those of the dispersed phase. It is therefore often possible to incorporate compounding ingredients into an emulsion that could not be effectively included into the dispersed phase alone because of incompatibility. The incorporation of powdered solids into a tough, infrangible binder such as rubber requires the expenditure of enormous power in heavy mixing equipment, besides causing a deleterious degradation of the binder. The dispersal of these same powders into an emulsion may sometimes be accomplished with a simple agitator or colloid mill if effective wetting and stabilizing agents are discovered, no degradation of the binder taking place.

For all the above reasons, emulsion processing and manipulation offer alluring possibilities. Development work is constantly in progress toward broadening the fields of application. Notable examples are water paints (Secs. 1441 *ff.*) and the latex processing of rubber (Sec. 1336). The operations of dipping and electrodeposition and the production of films, laminates, and expanded materials subsequently described in this chapter are very often effected with emulsions.

DIPPING

844. Dipping is a technique often employed for making coatings and thin-walled hollow objects. The binder and compounding ingredients

are either dissolved in a solvent or dispersed in an emulsion. The former is termed a *dope*, the latter a *latex*.

A form of the desired shape is dipped into the liquid and then withdrawn. After excess liquid has drained off, the volatile material is evaporated and the artifact is stripped from the form. The form is usually rotated during evaporation of the solvent. Proper control over evaporation is important. Forms must sometimes be coated to permit easy stripping. Redipping is frequently used to increase thickness.

ELECTRODEPOSITION

845. If a high-polymer binder is capable of being dispersed in a liquid medium in the form of charged colloidal particles, it is sometimes possible to make shaped articles by depositing the particles on an electrode. Rubber latex is a case in point. The process variables are difficult to control, and this method has not as yet enjoyed wide application.

PRODUCTION OF FILM

846. Thin transparent film is produced mainly for package wrapping, photographic film, sausage casing, lining, and sealing. Many high polymers, mainly of the thermoplastic type, are used for the purpose. Among them are viscose, cellulose acetate, cellulose nitrate, cellulose acetate-butyrate, ethyl cellulose, gelatin, rubber hydrochloride, synthetic polyamides, polyvinyl alcohol, polyvinyl butyral, polyvinyl chloride-acetate, and polymethyl methacrylate.

Several manufacturing techniques are employed, but the main ones may be divided into two categories, described in the two sections following.

847. Extrusions Similar to Synthetic-fiber Spinning. The mix is prepared and then extruded through a slit instead of through the fine holes of a spinneret, using techniques similar to wet, dry, or melt spinning. As a consequence, the product is a continuous thin film instead of a collection of fibers. Film mixes differ from fiber mixes in that they often contain considerable amounts of permanent external plasticizer to keep the finished film pliable.

848. Coating and Stripping of Highly Polished Surfaces. In this method a solution of the mix is fed continuously from a reservoir through a slit to the highly polished surface of a drum or continuous band moving at constant speed (Fig. 8-14). As the drum or band travels forward, the solvent is evaporated from the mix under very carefully controlled conditions. Eventually the sufficiently dried film is stripped off the drying surface and passes to a receiving roll. No standard procedure or conditions may be stated. They vary widely with the binder and the properties desired in the finished film.

The term *casting* is often used to describe any of the film processes outlined above. This unfortunate terminology is likely to be confusing to the uninitiated reader.

Techniques have been perfected for manufacturing thin films built up of layers of several kinds of polymers, each performing a special

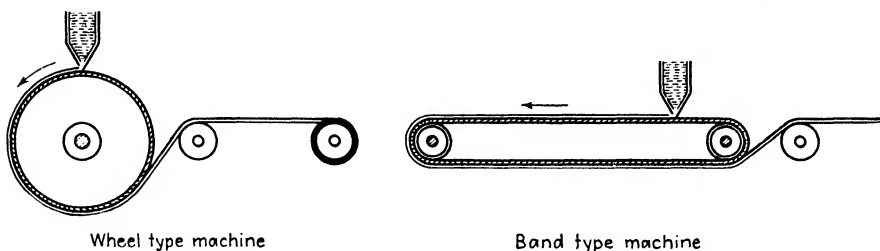


FIG. 8-14. Film-forming machines. (H. R. Simonds and C. Ellis, "Handbook of Plastics," D. Van Nostrand Company, Inc., New York, 1943.)

function. Three-, five-, and even seven-layered materials are produced. Often the outermost layers are applied in the form of lacquer.

PRODUCTION OF LAMINATES

849. In laminated products the filler is present as layers or sheets. Although their production involves no intrinsically novel molding methods, the laminates must be handled so differently that they must be separately considered. Their structural properties are outstanding. The very strongest products of the plastics and rubber industries are laminates, and it is mainly through them that high polymers invade fields of structural applications formerly reserved almost solely for the metals.

850. Laminating Materials and Procedures. Paper, light and heavy cotton and linen fabrics, asbestos paper, asbestos fabric, glass fabric, metal foils, and wood veneers are all used as laminations. Although thermoplasts are sometimes employed, the binders are more usually of the thermosetting type since the aim in laminate production is most often to attain high structural strengths and the latter binders impart greater rigidity and exhibit far less creep.

When the lamination is available as a practically endless pliable sheet, *e.g.*, paper or fabric, readily capable of absorbing a liquid, production is conducted as follows:

An A-stage resin or unvulcanized rubber is dissolved in a solvent or emulsified to form a dispersion of suitable viscosity. The filler is unwound from a roll and passes continuously through a trough, where it is impregnated with the polymer dispersion. It then passes between squeeze rolls or doctor blades, whose clearance is adjusted according to the amount of binder to be left in the product. (In an alternate method, the dispersion is applied to only one side of the sheet.)

The impregnated sheet may be passed through a heated drying tunnel to remove solvent and, in the case of thermosetting resins, to advance the polymerization to a nontacky B-stage. From this point on, the handling of the stack is determined by the physical shape desired in the finished product. If flat laminate is to be made, the correct number of sheets stacked one upon the other are simultaneously subjected to heat and pressure between polished plates, the binder curing or setting to a C-stage. To make tubes or hose, the stock is wound upon heated mandrels while under tension or pressure until the desired thickness has been built up. A so-called "rolled tube" is next baked in an oven at atmospheric pressure until the binder has cured. To make a molded tube, on the other hand, the assembly is cured in a mold under combined heat and pressure. Molded tubes are denser and stronger but show seams at the parting lines of the mold.

Solid laminated rods are often made by winding the impregnated filler on a very thin mandrel, which is withdrawn before molding. The center channel is filled up when pressure is applied. Rods may also be turned out of flat laminated stock if the stock is rigid and machinable.

Articles of irregular shape are often formed by cutting binder-impregnated sheets to pattern, then stacking and molding. Gears, bearings, and the like are often made in this way.

Since laminates have a "grain," they are anisotropic, their properties differing along different axes. Often a more even balance of strength is required, as in plywoods. To attain this, alternate layers of the filler are crossed at right angles to one another. The magnitude of the effect is shown in Table 9-10, page 377. When balanced strength in all directions is required, so-called *macerated laminates* are sometimes molded. A resin-impregnated sheet material is chopped into small pieces and then compression-molded like an ordinary molding mix. The resulting products have balanced strength that is fairly high, together with a high gloss finish.

When crossed wood layers are used as the lamination, the resulting product is called a *plywood*. Since wood is not available in very long sheets and since, even when it is sliced into veneers only $\frac{1}{48}$ in. thick, it is not nearly so pliable as paper or fabric and does not so readily absorb liquid, production methods must be modified (Sec. 941).

851. Decoration and Special Features. The top layer of an otherwise drab laminated product may be colored, or it may be a veneer of a rare or costly material. Or, for example, the lamination next to the top may be black and the outermost white with a pattern cut into it. By these and other means, beautiful decorative effects and costly surfaces may be obtained on laminated panels at relatively low expense. When urea-aldehyde binder and alpha-cellulose laminations are used, translucent laminates for lighting fixtures result.

Laminated paneling for the tops of restaurant tables and bars often has a metal lamination near the surface to conduct away the heat from burning cigarette stubs and prevent marring of the finish.

Structural material of controlled, graded density may be produced as illustrated in Fig. 8-15. Such a laminate is useful for making airplane propellers. Many other unique features and combinations are possible in laminated products.

852. High-pressure and Low-pressure Laminates. The pressure applied during molding affects both the manufacturing cost and the properties of the finished product. The thermosetting binders used in the production of the early plastic laminates were such that relatively high molding pressures, that is, 250 to 2,000 psi or more, were required.

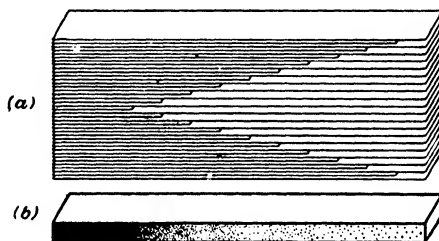


FIG. 8-15. Differential density laminate for airplane propeller. (a) Assembly before hot pressing. (b) After pressing to uniform thickness. (Courtesy of Resinous Products and Chemical Co.)

High temperatures ranging from 300 F upward were likewise necessary. Hot-pressed laminates of this kind are still manufactured in great quantity and have the best properties for many applications.

However, the range of useful properties in laminates has been greatly extended by the subsequent development of thermosetting binders that have made it possible to mold and cure laminates at pressures of $\frac{1}{2}$ to 300 psi and temperatures as low as 70 F. These are the so-called "low-pressure" laminates. Low-pressure molding, then, is molding performed at pressures ranging from a simple contact pressure of 1 psi or less to a maximum of about 300 psi (usually less). For this work, it is highly desirable to have the binders in liquid sirup or emulsion form. Those most extensively used at the moment are phenol-, urea-, thiourea-, and melamine-aldehydes and thermosetting ester resins. They may be classified as shown in Table 8-9. Many of the room-temperature and warm-setting types were originally developed for the plywood industry. They are made by keeping the resin molecules small (for high solubility and ready impregnation of the sheet stock) and by incorporating catalysts and hardeners of kinds and in amounts that result in setting of the binder at the low working temperatures and pressures.

TABLE 8-9. GENERAL TYPES OF RESINS USED IN LOW-PRESSURE MOLDING

Resin class	Setting type	Hardening temperature, deg F	Molding time*	Molding pressure, psi
Phenol-aldehyde.....	Room temperature	70-140	30 min-12 hr	1-75
	Warm-setting	140-220	15 min- 2 hr	1-250
	Hot-setting	280-360	5 min- 1 hr	1-250
Urea-aldehyde.....	Room temperature	70-140	10 min- 4 hr	1-75
Thiourea-aldehyde.....	Warm-setting	140-220	5 min-15 min	1-200
Melamine-aldehyde.....	Hot-setting	260-300	5 min- 1 hr	150-250
Thermosetting ester....	Warm- or hot-setting	140-325	5 hr-2 min	1-2

WILSON, F. P., N. D. HANSON, and W. S. LARSON, "Plastics Catalog," Plastics Catalogue Corp., New York, 1944.

* The longer hardening periods generally refer to the rubber bag-autoclave process.

Much low-pressure molding is done with one rigid mold member constructed of wood or metal and one flexible mold member consisting of an inflatable rubber bag. Figure 8-16 shows a setup for molding one entire

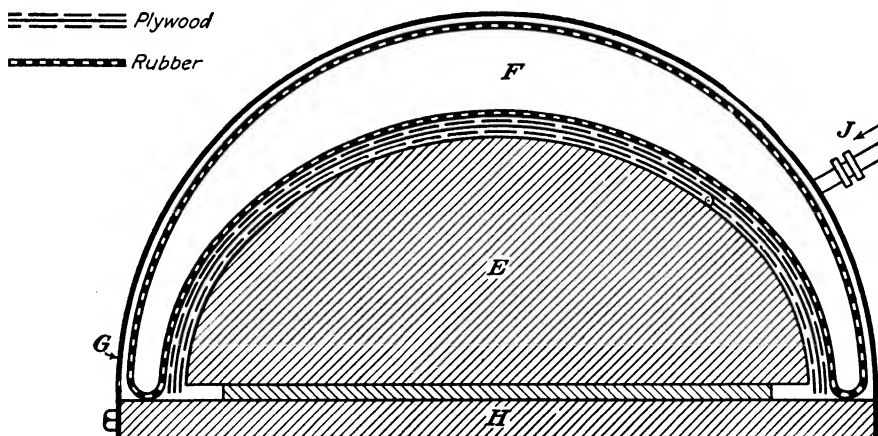


FIG. 8-16. Molding a half fuselage by flexible-bag low-pressure molding technique. *E*, inside mold. *F*, rubber bag, inflated through inlet *J*. *G*, outer steel shell, bolted to base *H*. (Courtesy of Resinous Products and Chemical Co.)

half of a plastic-plywood airplane fuselage. The inside mold member *E* is rigid, being made of metal or wood. A layer of thin wood veneers is assembled over this member. The veneers must be stapled or otherwise fastened into position to maintain the curvature of the surface. Next comes a generous application of low-pressure-molding resin. This may be applied by brush or spray if it is in liquid form. Or, to facilitate handling, thin sheets of paper heavily impregnated with the binder may

be laid down. Then comes a second layer of wood veneer placed with the grain running at an angle to the first layer. This is followed by another layer of binder, and so on, until the assembly has been built up

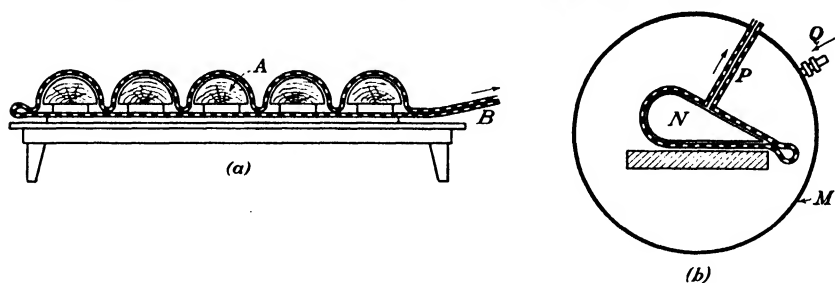


FIG. 8-17. Flexible-bag molding techniques. (a) Molding with vacuum bags. A, solid wood pilasters to be veneer-faced. B, vacuum exhaust outlet. (b) Molding subassembly parts in vacuum tank. M, outer steel tank. N, subassembly inside rubber bag. P, vent to atmosphere or vacuum connection. Q, pressure connection for steam. (Courtesy of Resinous Products and Chemical Co.)

to the desired thickness. Over the topmost layer of the assembly there is placed a porous cloth, cellophane, or other "blanket" to prevent squeezed-out binder from sticking to the flexible bag. The latter is put

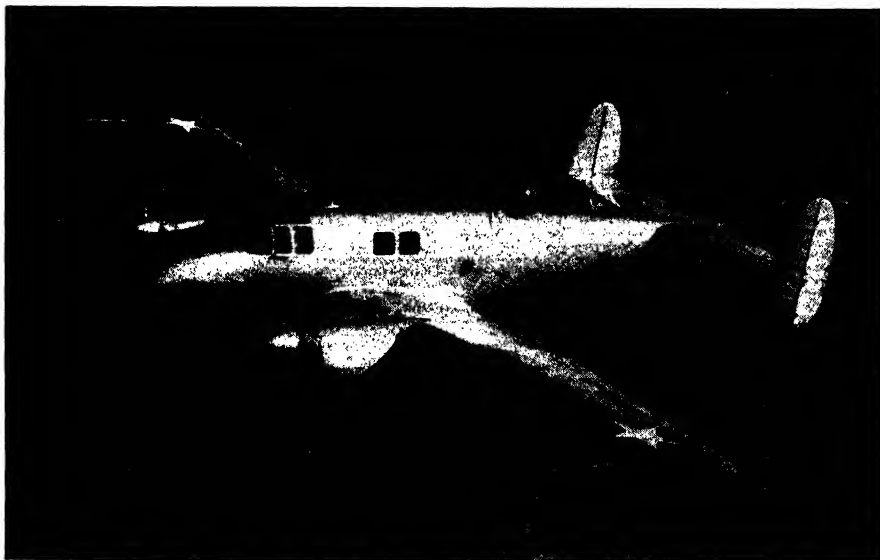


FIG. 8-18. Plane (AT-21) built of plastic plywood molded by the Duramold process. (Courtesy of Fairchild Aircraft Div., Fairchild Engine and Airplane Corp.)

into position, and the mold is then closed by bolting a steel shell to the heavy base H. Heat and pressure are then applied by inflating the bag through inlet J with steam, air and steam, or hot water until the cure is finished.

Regardless of the curvature of the piece, the pressure is thus applied uniformly and normal to the surface of the assembly. The finished piece is practically free of internal stress and shows little tendency to warp or delaminate. Other methods for applying the flexible-bag technique are shown in Fig. 8-17.

All sorts of combinations of thermosetting binders and laminated fillers, including high-strength paper and woven glass cloth, are used to produce curved pieces, often of very large size (Fig. 8-18).

PRODUCTION OF EXPANDED MATERIALS

853. An expanded material is a solid uniformly permeated with voids or cells that occupy an appreciable fraction of the total volume. Wood and sea sponges are natural examples. The production of new synthetic expanded materials during the Second World War represented a major development in the high-polymer field. These materials find applications as sponges, cushions, thermal insulation, sound-absorbing materials, and low-density materials of construction. They may be of hard and soft vulcanized rubbers or plastics of both the thermoset and thermoplast types.

The nature of the porosity is of prime importance, three main factors being involved: (1) the size of the individual cells; (2) the ratio of cell space to total volume; (3) the continuity or discontinuity of the cells. These determine the permeability, apparent density, strength, thermal insulating value, etc.

In terms of the third factor, expanded materials are divisible into two basic kinds, *open-cell* and *closed-cell* structures. For example, an expanded soft rubber of the open-cell variety where the cells are interconnected is capable of absorbing large quantities of liquid and thus serves as a sponge. On the other hand, a buoy or pontoon material must not become waterlogged. It must be of the closed-cell type where each void is a separate, sealed hole.

In the manufacture of expanded synthetics all three porosity factors must be kept under close control in order to obtain materials of uniform apparent density and cell structure. The art is often reminiscent of the leavening of breadstuffs. Only a few of the several techniques will be discussed.

A thermosetting resin or vulcanizing rubber mix is exposed to a gas such as nitrogen under pressure high enough to cause a certain amount to dissolve in the mix. Molding or vulcanizing is then started. After partial curing the external pressure is lowered, permitting the absorbed gas to expand and form thousands of nonconnected closed voids. The cure is then completed. If the resulting closed-cell product is an expanded

soft rubber vulcanizate, it may be converted to an open-cell structure merely by passing it through a mangle. This breaks the walls of the closed cells and makes them interconnecting.

Emulsions and latices lend themselves well to the manufacture of expanded products by several techniques. In one, air is whipped in to form a foam much after the manner of beating egg whites. This foam is then stabilized, gelled, and cured. The leavening may also be accomplished by the addition of a blowing agent, a compounding ingredient that decomposes on heating with the liberation of gas.

One method of making expanded thermoplasts is to incorporate a blowing agent and extrude the mix through a hot die. The resulting product may be either rigid or pliable.

A high-polymer emulsion or solution of sirupy consistency may be mixed with catalyst and blowing agent just prior to use, so that the final mixture is both self-rising and self-curing. Shortly after mixing, polymerization or cross-linking starts. The liberated heat of reaction decomposes the blowing agent (*e.g.*, sodium bicarbonate), causing the mass to foam while curing. By this technique the expanded product may be formed *in situ*.

Included among available expanded materials are hard and soft natural and synthetic rubbers, phenol-aldehyde and urea-aldehyde resins, polystyrene, plasticized polyvinyl chloride, and regenerated cellulose (viscose). Strong materials with apparent densities of 1 to 2 lb per cu ft are readily produced. These are only one-fourth to one-tenth as dense as cork or balsa wood. Their structural applications are discussed in Chap. 9. Some possess outstanding insulating properties, combining light weight and low thermal conductivity with moisture resistance, nonsettling, and low flammability (Table 10-3, page 454).

FORMING

854. Forming usually consists in bending and drawing flat sheet stock into objects having simple or compound curves. The flat stock is raised to a suitable temperature by either dry heating or immersion in a hot liquid, after which it is shaped by applying pressure by means of a die or, in some cases, by merely draping over a suitable jig.

Forming may be applied to any typical thermoplast, and for a long time the notion persisted that fully cured thermoset materials such as laminated and compression-molded phenoplasts could not be formed. However, this is not so. In the normal hot compression molding or high-pressure laminating of phenoplasts, the mix is heated to 280 to 360 F, and cross-linkage occurs. Nevertheless, if the resulting fully cured material is heated rapidly to a temperature of 350 F or more (temperatures well

above 400 F are common in practice), it creeps and relaxes sufficiently rapidly to be formed successfully, as may be seen from Fig. 8-19. While in the heat-plasticized condition, sharp bends and elongations of as much as 10 per cent or more may be effected on a canvas laminated phenoplast. The fabric, not the thermoset binder, limits the extensibility.

This forming of mutaplasts is variously called *postforming* and *thermoelastic forming* and is ordinarily applied to laminates. Although probably applicable to all thermoset materials, data at the current writing are available only on phenolic resin products. The flat stock is heated rapidly to 400 F or more for a few minutes and then formed in a cold die



FIG. 8-19. Postformed dome light mounting bracket. [W. I. Beach. *Mech. Eng.*, **65**, 719 1943).]

at low pressures. Expensive high-pressure hot-pressing equipment is eliminated. Costs are low and production is rapid.

The best mechanical properties in the final product are obtained if fully cured stock is used. Undercured starting stock is definitely undesirable. Stock with a 200 per cent overcure, *i.e.*, stock that has been cured three times as long as normal in the original hot pressing, can be postformed just as readily as normally cured material.

If maintained for too long a time, the high temperatures employed in postforming will cause blistering or thermal decomposition of the resin or filler, but the materials may normally be reformed several times. An interesting feature of the process is that many mechanical properties such as Young's modulus and tensile, flexural, and yield strengths are, if anything, moderately improved. However, shear and impact strengths drop somewhat. After-polymerization and rearrangement and realignment of binder and filler are probably among the causes of these changes.

When a metal is formed, the thickness at a sharp bend or fairly deep draw decreases. Surprisingly, with canvas laminated phenoplast it remains constant or actually increases slightly. This is in line with the fact that postforming results in an increased water absorption, *e.g.*, an

increase from 2 per cent before to 6 per cent after for the above-mentioned material.

REFERENCES

GENERAL

DAVIS, R. L., and R. D. BECK, "Applied Plastic Product Design," Prentice-Hall, Inc., New York.

SOCIETY OF THE PLASTICS INDUSTRY, "SPI Handbook," New York.

See also Appendix A, particularly Secs. A-6 and A-7.

PARTICULAR TOPICS

See references accompanying tables and figures of this chapter.

Design and Construction of Plastic Molds

DuBOIS, J. H., and W. I. PRIBBLE, "Plastics Mold Engineering," American Technical Society, Chicago.

THAYER, G. B., "Plastics Molds," Huebner Publications, Cleveland.

Injection Molding

THOMAS, I., "Injection Molding of Plastics," Reinhold Publishing Corporation, New York.

Production of Laminates

HICKS, J. S., and FRANCIS, R. J., "Low Pressure Laminating of Plastics," Reinhold Publishing Corporation, New York.

CHAPTER 9

MECHANICAL PROPERTIES

In this chapter it will be shown how mechanical properties correlate with chemical composition, molecular and gross structure, and rheological behavior and the manner in which they are influenced by manufacturing procedure and external conditions such as temperature and humidity.

ELASTIC MODULUS AND TENSILE STRENGTH

When a new material is being developed or introduced for making fibers, films, or molded artifacts, one of the first inquiries made concerns its tensile strength and elastic modulus. These are by no means the only important strength properties, but they are used as a general guide to other structural attributes.

900. Calculations of Elastic Modulus and Tensile Strength from Theory. Consider a straight, planar zigzag hydrocarbon chain (Fig. 9-1). If tension were applied to the ends, two types of elastic deformation could take place. Either the valence angle α or the bond length d could be increased. One cannot, of course, apply a measured load to a single molecule to observe its elastic behavior, but from infrared and Raman spectra it is possible to calculate two values for the elastic modulus of the molecule, one involving increase of the valence angle and the other the stretching of the bonds. The smaller of the two would be expected to be the controlling value

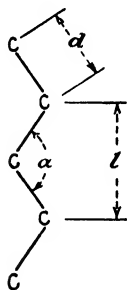


FIG. 9-1. Dimensional relations in saturated aliphatic chains; $d = 1.547 \text{ \AA}$, $l = 2.54 \text{ \AA}$, $\alpha = 109^\circ 30 \text{ min}$.

in an actual deformation. This turns out to be the one involving the distortion of the valence angle.

If complete detailed knowledge of the architecture and dimensions of a molecule are available from x-ray analysis, as well as the way in which the molecules are arranged in a crystallite, the elastic modulus of the perfect crystallite can be calculated. Working from the known structure of cellulose as revealed by x-ray studies, Meyer and Lotmar calculated the elastic modulus of cellulose and found it to be between 11×10^6 and 17.5×10^6 psi. One would expect this to be a limiting value since the calculations are made on the assumption of perfect chain alignment. Experimental values for real cellulose fibers are listed in Table 9-1. It

will be seen that the modulus increases as the degree of crystallinity increases and that for well-oriented fibers such as flax, hemp, and ramie the experimental values approach the calculated value closely. Similar good agreement has been obtained for other fibers.

TABLE 9-1. ELASTIC MODULI REPORTED FOR FIBERS AND FILMS

Material	Elastic modulus in tension		
	Dynes/ sq cm ($\times 10^{-11}$)	kg/sq mm	psi ($\times 10^{-6}$)
Cotton, native.....	0.2-0.8	200-800	0.28-1.14
Flax, native.....	8-11	8,000-11,000	11.4-15.7
Hemp, native.....	6-8	6,000-8,000	8.5-11.4
Ramie, native, dry.....	5-7	5,000-7,000	7.1-10.0
Ramie, native, wet.....	1.9	1,900	2.7
Ramie, native, mercerized.....	8.2	8,200	11.7
Highly stretched viscose rayon, bone-dry....	4.5	4,500	6.4
Highly stretched viscose rayon, air-dry.....	3.3	3,300	4.7
Normal viscose rayon, bone-dry.....	1.47	1,470	2.1
Normal viscose rayon, at 50 C.....	1.57	1,570	2.2
Normal viscose rayon, air-dry.....	1.15	1,150	1.6
Normal viscose rayon, wet.....	0.135	135	0.19
Acetate rayon, air-dry.....	0.6	600	0.85
Acetate rayon, wet.....	0.17	170	0.24
Silk, air-dry.....	1.44	1,440	2.1
Nylon, 50 % R.H.....	0.3	300	0.42
Cellophane film.....	1.0	1,000	1.4
Cellulose nitrate film.....	0.5	500	0.71
Cellulose acetate film.....	0.4	400	0.57

Data from several sources, notably

MARK, H., in "Cellulose and Cellulose Derivatives," E. ORT, editor, Interscience Publishers, Inc., New York, 1943.

The calculation of tensile strengths is less fruitful, for reasons indicated in Sec. 712. It was pointed out that theoretically calculated tensile strengths, even of simple crystalline substances, are far below real values owing to the existence of notches and flaws (crystal imperfections). For a high-polymer fiber, several different limiting values may be calculated based on different assumptions regarding the arrangement of the chain molecules in the mass. Mark has performed such calculations on cellulose. The first assumption is a fiber consisting of infinitely long cellulose molecules all perfectly parallel to one another in a perfect crystal. The breaking of such a fiber would involve the rupture of primary bonds. For this case, Mark obtains a theoretical tensile strength (tenacity) of 2,000,000 psi (105 g per denier).

In a second calculation, it is assumed again that the specimen consists of perfectly parallel chains, this time of finite length and overlapping each other irregularly as shown schematically in Fig. 9-2a. In such a mass a minimum tensile value will be found if at some point in the sample there is a cross section at which no chain overlapping occurs (Fig. 9-2b). The specimen would break in tension by the rupture of secondary valence bridges. Using as a basis of calculation a secondary valence force of

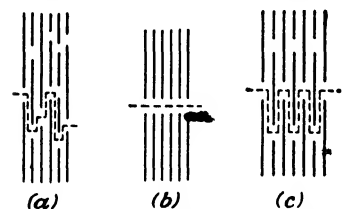


FIG. 9-2. Schematic representations of parallel chain molecules. (a) Random overlapping. (b) No overlapping. (c) Regular overlapping.

4 to 5 kcal per g mole, the tensile strength at such a section is 38,000 psi (2 g per denier), which is in good agreement with the actual tensile strength of poorly oriented viscose rayon filaments (Table 9-2).

To account for the considerably higher tensile strengths found in many real cellulose fibers (Table 9-2 and Appendix B), all that is necessary is to recall that the probability of finding a cross section such as that of Fig. 9-2b is slight and that the probability decreases as the average chain length and the degree of orientation increase. Lower tensile values (lower than 38,000 psi) are also readily accounted for by assuming imperfect chain alignment (less chains passing through unit cross section).

By assuming an idealized system of regularly overlapping, completely parallel chains (Fig. 9-2c) having a uniform degree of polymerization of 400, and assuming further that the mass will fail by *slippage* of the chains past one another against secondary valence forces, Mark arrives at a calculated tensile strength of 190,000 psi (10 g per denier), which is 50 per cent higher than the tensile strength of highly oriented regenerated cellulose fibers and strong natural samples of flax or hemp. (For this calculation an activation energy of slippage identical with that during viscous flow was used, *viz.*, a force of 10^{-1} dynes between —OH groups on neighboring cellulose chains.)

Several points emerge from the above discussion. The limiting value of 2,000,000 psi for the tensile strength of a "perfect cellulose fiber" is valuable in setting the upper limit to what might be accomplished in technological development. All the other calculations of tensile strength are inadequate attempts to evaluate the effect of flaws; and, by making various assumptions about the arrangement of the chains in the high-polymer mass, we can arrive at almost any value for the tensile strength. It should be borne in mind that the best available knowledge indicates strongly that the molecular arrangement in a fiber is actually as shown in Fig. 2-9, page 55. It is correct to say that in the present state of our

knowledge the calculation of real high-polymer strengths is not a problem in molecular theory, but rather one for a "theory of imperfections" which has not as yet been developed to a point where real strengths may be estimated to the degree of accuracy we should like to attain. However, it does appear likely that rupture of a fiber in tension is more a matter of overcoming secondary valence bridging than the breaking of primary valence bonds.

The qualitative concepts emerging from the discussion are valuable. Using the concept of chain overlap in the direction of the fiber axis, at low average D.P.'s the amount of this overlap would be small, and the mass would rupture easily. At very high degrees of polymerization, not only would the tensile strength be higher, but it is at least conceivable that rupture might involve the breakage of primary valence links. At any rate, the tensile strength along the fiber axis should be much higher than that across it since tension at right angles to this axis would be resisted only by secondary valence forces acting in parallel, whereas tension along the axis of orientation would be resisted by secondary valence bridges acting in series, or even by primary valence bonds. From the flaw concept it follows that the strength at various cross sections of a fiber will differ. The magnitude of the effect may be demonstrated by starting with long fibers and subjecting them to repeated breakage. Peirce and coworkers found that the average tensile strength of cotton fibers at the third break was double that at the first, while at the sixth break it was triple.

901. Factors Affecting the Tensile Strength of a High Polymer. In previous discussion throughout the text, qualitative and theoretical statements have been made that this or that factor should influence the strength of a material in a certain way. In many instances the reader was asked to accept these statements on faith. It is essential to the treatment developed in this text to present sufficient experimental evidence and data to substantiate the theory and show the magnitudes of the several factors. This is done in the sections that follow.

902. Specific Molar Cohesion and Average Molecular Weight. Before a linear-polymeric material attains any appreciable mechanical strength in terms of usual methods of measurement, a certain minimum degree of polymerization must be reached. This minimum varies inversely as the specific molar cohesion and ranges from about 40 for the polyamides, where the intermolecular attractive forces are high, to about 80 in the polyhydrocarbons, where these forces are low (Table 2-11, page 46). For other polymers the values lie in between.

Once the critical value has been reached, increase in the degree of polymerization is accompanied by roughly proportional increase in the

tensile strength until the former attains a value of about 200 to 250 (Fig. 9-3). Thereafter the slope of the curve grows more gradual; and when an average degree of polymerization of 600 or 700 has been reached, the curve has plateaued off to such an extent that further increase in the chain length has practically no effect on the strength. Not only the critical minimum value but also the slope of the curve and the maximum strength value are dependent upon the inherent intensity of the intermolecular attractive forces. As pointed out previously, this curve is similar in form to those obtained when other properties reasonably attributable to inter-

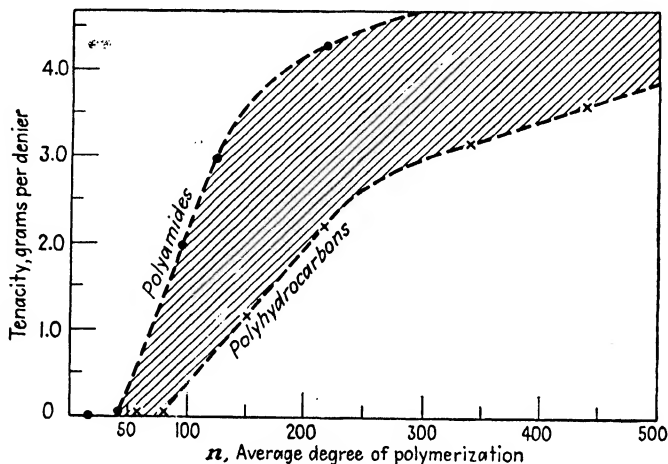


FIG. 9-3. Tensile strength of high polymers as a function of degree of polymerization. [H. Mark. *Ind. Eng. Chem.*, **34**, 1343 (1942).]

molecular attractive forces are plotted against degree of polymerization (Figs. 2-5 and 2-6, page 45).

903. Orientation and Crystallization. The slope of the curve in Fig. 9-3 is steeper if orientation or crystallization is favored during manipulation of the material. This is to be expected on theoretical grounds. Indeed, one may generalize to state that any factor which increases the forces of attraction between chain polymers results in a steeper slope. The effects of orientation upon the tensile strengths of some cellulosic fibers and films are shown quantitatively in Tables 9-2 and 9-3.

904. Molecular-weight Distribution. Several studies have been made of the relation between mechanical properties and the molecular-weight distribution curve. The results appear to indicate that a definite correlation between mechanical properties and the shape of the distribution curve is doubtful but that the presence of as little as 10 to 15 per cent of low-molecular-weight fractions (having D.P. values below 100 to 150) acts adversely on all mechanical properties, *e.g.*, tensile strength and folding strength.

TABLE 9-2. INFLUENCE OF ORIENTATION ON FIBER TENACITY

Fiber	Condition	Tenacity	
		g/denier	psi
Viscose rayon.....	Poorly oriented	1.7 to 1.9	33,000 to 37,000
	Moderately oriented	2.0 to 2.6	38,000 to 50,000
	Highly oriented	3.0 to 3.5	58,000 to 67,000
	Extremely oriented	Up to 5.8	Up to 111,000
Acetate rayon.....	Poorly oriented	1.3 to 1.6	22,000 to 27,000
	Moderately oriented	1.8 to 2.3	31,000 to 39,000
	Highly oriented	3.5 to 4.0	60,000 to 68,000

MARK, H., in "Cellulose and Cellulose Derivatives," E. OTT, editor, Interscience Publishers, Inc., New York, 1943.

TABLE 9-3. INFLUENCE OF STRETCHING OF A CELLOPHANE FILM ON ITS TENACITY ALONG DIFFERENT AXES

Angle between the direction of stretching and a given direction in the film, deg	Tenacity			
	Before stretching		After stretching	
	kg/sq mm	psi	kg/sq mm	psi
0	11.6	16,500	26.5	37,500
30	11.2	15,900	15.7	22,300
60	11.4	16,200	10.2	14,500
90	11.5	16,400	4.5	6,400
120	11.9	16,900	9.3	13,200
150	11.2	15,900	14.7	20,900
180	11.1	15,800	25.9	36,900

MARK, H., "Physik und Chemie der Cellulose," Verlag Julius Springer, Berlin, 1932.

905. Flaws Distributed along the Length of a Fiber. Since a fiber or yarn will break at its weakest point, a point representing a flaw or imperfection, it would appear likely that the tenacity on the average would decrease as the length of the test samples increased, since the probability of the occurrence of a flaw would increase with the length (Table 9-4).

Assume a fiber of length l and tenacity t . Assume further that the average frequency of flaws along the fiber is given by a coefficient α . If the fiber is now increased by a length dl , a decrease in tensile strength $-dt$ may be expected and a reasonable function describing this loss will be

$$-dt = \alpha \frac{dl}{l} \quad (9-1)$$

since the probability of already having a flaw is proportional to l , while that of introducing a new flaw is proportional to dl .

If l_s is a standard test length or a shortest sample length conveniently handled in actual testing and t_s is the average tenacity corresponding to this length, then, by integrating Eq. (9-1)

$$t_l = t_s - \alpha \ln \frac{l}{l_s} \quad (9-2)$$

The plot of the observed tenacity t_l against $\ln (l/l_s)$ is a straight line whose slope is α and whose intercept is the maximum obtainable tensile strength or the *substance strength*.

TABLE 9-4. INFLUENCE OF LENGTH ON TENSILE PROPERTIES OF GLASS FIBERS
(Fiber diameter constant at 13μ)

Length of test fibers, in.	Average ultimate tensile strength, psi	Elongation at break, %	Modulus of elasticity, psi $\times 10^{-6}$
0.000	223,000 (extrapolated)	14.5 (extrapolated)	
0.197	210,000	6.1	2.8
0.394	200,000	4.3	4.9
0.787-0.790	185,000	3.1	5.2
1.72-1.77	162,000	2.3	6.3
3.54	142,000	1.9	4.7
7.20	124,000	1.7	6.3
61.5	103,000		
Infinite	100,000 (extrapolated)		

ANDEREGG, F. O., *Ind. Eng. Chem.*, **31**, 290 (1939).

TABLE 9-5. INFLUENCE OF DIAMETER ON TENSILE STRENGTH OF GLASS FIBERS
(Fiber length held constant)

Diameter of Test Fibers, in.	Ultimate Tensile Strength, psi
0.00075	100,000
0.00060	125,000
0.00050	150,000
0.00040	185,000
0.00030	250,000
0.00020	395,000
0.00010	890,000

ANDEREGG, F. O., *Ind. Eng. Chem.*, **31**, 290 (1939).

Measurements of different fibrous materials of varying sample lengths yield experimental data in good agreement with Eq. (9-2). The data show that fibers and yarns of different manufacturing history and different source have appreciably different α values, so that the method is useful for estimating freedom from flaws and relating this to manufacturing techniques. Peirce and his coworkers found that in the case of Sakel cotton hairs the average tenacity for 1-mm specimens was 60 per cent greater

than those for 10-mm specimens; for Zaria cotton hairs, the 1-mm specimens were 90 per cent stronger. Analogously, the strength of adhesive joints drops with increased thickness of adhesive layer (Table 15-1, page 641).

906. Flaws Distributed over the Cross Section. The probability of the occurrence of flaws on a cross section increases with the cross-sectional area. The potency of this effect is shown in Table 9-5.

If the tenacities are determined for a large number N_0 of fibers all having the same length, the tenacity values are found to lie along a distribution curve similar to that of Fig. 9-4, although usually somewhat

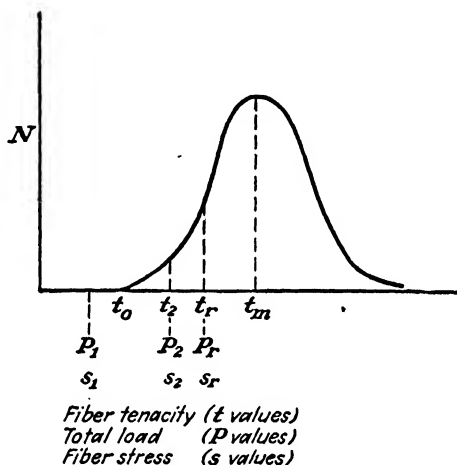


FIG. 9-4. Tenacity distribution curve for a bundle of fibers.

skewed toward lower tenacities. In this figure, t_0 is the tenacity of the weakest fiber, and t_m is the mean value for all the fibers. Assume that a bundle is made up of perfectly parallel fibers all of the same length and of uniform cross section A . If a tensile load P is applied such that none of the fibers in the bundle breaks, the load will be borne by all the fibers, each of which will be under the same stress s , so that

$$s_1 = \frac{P_1}{N_0 A} \quad (9-3)$$

As long as s_1 is lower than t_0 , this will continue to be the case and the fibers of the bundle will be stretched without rupture.

If, however, the load is increased to P_2 , all the fibers having tenacities below t_2 will break and the total load must be borne by the remaining fibers. In other words, the total load P_2 must be divided, not by the whole area, but by the area with tenacities from t_2 to infinity; *i.e.*, the actual tension in the fibers will be, not

$$s_2 = \frac{P_2}{N_0 A}$$

but

$$s_2' = \frac{P_2}{N_2 A} \quad (9-4)$$

Eventually a load P_r is reached for which the fibers breaking under each increment of tenacity impose so much additional tension on the next ones that rupture becomes continuous and the whole sample breaks. At this point the breaking tension of the bundle is s_r , which equals t_r .

If a function for the distribution curve has once been determined experimentally, the bundle breaking strength may then be calculated. The value of t_r is always considerably lower than t_m , the mean tenacity of single fibers. For example, Peirce and his coworkers found that the tensile strength for bundles of 50 cotton hairs was only 39 per cent that of the mean tenacity for single hairs. Since cords, ropes, and the yarns of which textiles are woven are, in effect, fiber bundles, the basic importance of the above considerations will be realized. (Fiber-bundle tests are a quicker and more reliable means than single-fiber tests for obtaining reliable technical tensile values.)

It is important to note that, just as a yarn or fiber bundle breaks via progressive failure of successive fractions of its fibers, so also does a single fiber break by progressive failure of its fibrils and probably a single fibril in turn by progressive failure of its chain molecules, most probably in the amorphous regions.

907. Twist. The strengths of cellulosic single fibers having varying degrees of natural spirality, or twist, among their fibrils are presented in Table 9-6. It is evident that with increased spirality there is a loss in strength. There is a similar correlation between the strengths of fiber bundles and the degree of twist (Table 9-7). An obvious explanation is that the axis of alignment is at an angle to the direction of tensile loading so that only a component of the strength is available for resisting the load.

TABLE 9-6. SPIRALITY AND TENSILE STRENGTHS OF NATURAL CELLULOSIC SINGLE FIBERS

Single fiber	Average angle of spiral, deg	Single-fiber strengths, kg/sq mm
Hemp.....	0	80-92
Ramie.....	3.5	70-80
Flax.....	5.5	69-110
Cotton.....	>50	28-44

TABLE 9-7. CHANDLER BUNDLE STRENGTHS WITH VARYING DEGREES OF TWIST

Fiber	Turns per in.	Tensile strength, psi	Loss in strength, %
Cotton.....	0	97,000	0
	2.29	93,750	3.4
	4.92	85,100	12.3
	8.00	68,950	28.9
	11.63	46,550	51.0
Rayon.....	0	29,200	0
	1.6	27,900	4.5
	3.2	26,500	9.2
	5.33	27,000	7.5

CONRAD, C. M., and E. E. BERKLEY, *Textile Research*, **8**, 341 (1938).

From these data it is concluded that twist in fiber bundles or other parallelized chain-unit masses is a source of weakness. Nevertheless, thread, yarn, cordage, and rope are all, in effect, twisted fiber bundles. If the fibers are not twisted together, they slip and pull out instead of helping to bear the tensile load. Twist is essential to gain fiber cohesion. Hence twist has two opposing effects on yarn strength. Longer fibers require less twist, and a higher percentage of them pass through any given cross section. For these reasons long-staple cotton makes stronger yarn than short-staple. In a well-made cotton yarn, about 70 per cent of the fibers actually break during rupture; but, owing to twist and the distribution factor, not more than 50 per cent of the single-fiber strength is ever realized in the yarn.

908. External Plasticization. External plasticization invariably decreases consistency and elastic modulus, showing clearly that the fundamental effect is a weakening action. One might expect that external plasticization would always decrease the tensile strength, too. Nevertheless, the tensile strengths of some fibers and brittle plastics are increased by the addition of judicious (not too large) amounts of plasticizer. For example, Appendix B shows that the wet strength of fibers (externally plasticized with water) is in some cases lower than the dry strength but in others notably higher. The phenomenon may be explained as follows:

Tension tends to straighten and align the chains or crystallites of a high-polymer mass. Such alignment would improve the closeness of packing and increase the attractive forces. Also, if such alignment could occur, especially in amorphous regions (Fig. 2-9, page 55), more chains could participate simultaneously in resisting the externally applied stress, *i.e.*, the external stress would be distributed more evenly among the structural elements of the mass. Both these factors would tend to

increase the tensile strength. However, if the consistency of the mass were too high, the external Brownian motions of the molecular chain segments and the motions of whole chains or crystallites with respect to one another might be so highly restricted that alignment could not take place. External plasticizer in proper amount might overcome these difficulties by lowering the consistency.

TABLE 9-8. INFLUENCE OF HUMIDITY ON TENSILE BEHAVIOR OF COTTON
Single Fibers of Sakel Cotton
(Mean of 200 tests)

R.H., %	Extension at break, %	Breaking load, g	Increase over breaking load at 10 % R.H., %
10	5.3	3.5	
30	6.7	4.2	20
50	8.0	5.1	46
65	8.8	5.3	51
80	9.2	5.3	51
90	9.3	5.3	51
100	9.4	5.3	51

BROWN, K., J. C. MANN, and F. T. PEIRCE, *J. Textile Inst.*, **21**, T186 (1930).

Cotton Yarn

R.H., %	Extension at break, mm	Breaking load, g	Increase over dry breaking load, %
0	22 (extrapolated)	160 (extrapolated)	
30	23	186	16
50	29	195	22
70	31	207	29
85	35	214	34
92	35	217	36
100	35	218	36

PEIRCE, F. T., and R. J. STEPHENSON, *Shirley Inst. Mem.*, **5**, 239 (1926).

To summarize, one may assume that external plasticization brings into play three main effects:

1. A lowering of the resistance to tension, due to the fundamental decrease in intermolecular forces brought about by plasticizers in general
2. An increased resistance to tension attributable to better alignment of the molecules or larger structural elements of the mass
3. An increased resistance to tension attributable to better distribution of the applied load, *i.e.*, the relief of localized internal stress by the participation of more structural elements in resisting the external stress

Whether the ultimate tensile strength increases or decreases in a

particular case will depend on whether factor 1 prevails over factors 2 and 3, or vice versa.

In a fiber the alignment of fibrils rather than molecules may be the more important consideration since both the molecular and gross organization of the material are determinants of its behavior. On the other hand, the behavior of yarns depends on the alignment and limited slippage of whole fibers.

The plasticizing effect of the humidity of the atmosphere is so important that the mechanical testing of many polymeric products is conducted under closely specified humidity conditions. Thus, for fiber testing the conditions are 65 per cent relative humidity at 21 C (70 F), while for paper testing the standard atmosphere is 50 per cent relative humidity at 23 C (73 F). Quantitative data on the effect of humidification for a specific case, cotton, are presented in Table 9-8.

909. Cross-linkage. The introduction of primary-valence cross-links invariably increases stiffness, creep resistance, and consistency, showing that the fundamental effect is mechanical reinforcement. Nevertheless, the effect on tensile strength is not always in the same direction.

Wool is a unique material in that its mechanical properties are intermediate between those of typical fibers and rubbers. The main chains have a low order of molecular symmetry and retract spontaneously and reversibly from elongations of as much as 100 per cent (Sec. 529). The main chains are joined to one another by cystine cross-links. Techniques have been developed for breaking these cross-links and remaking part or all of them in processes that may be controlled quantitatively [Eqs. (4-50), (4-51), and (4-53)]. The effects of primary-valence cross-linkage on wool are shown in Fig. 9-5, where the loading-unloading cycle of normal wool is compared with that of wool in which five-sixths of the cystine linkages have been broken by reduction and alkylation [Eqs. (4-50) and (4-51)]. The tensile stress required to produce a 30 per cent elongation is four times as great in the normal wool. The elimination of cross-links leaves the wool in a rubbery condi-

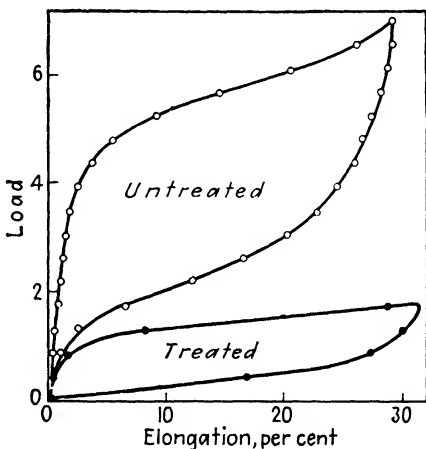


FIG. 9-5. Stress-strain cycle of wool before and after opening five-sixths of the cross-linkages by reduction and alkylation with methyl iodide. [M. Harris, L. R. Mizell, and L. Fourn, *Ind. Eng. Chem.*, **34**, 833 (1942).]

tion, and the differences in stress-strain behavior between the treated and untreated wool resemble those between unvulcanized and vulcanized rubber. Compare Fig. 9-5 with Fig. 13-12, page 576. By restoring progressively larger numbers of cross-links via Eq. (4-53), the stress-strain behavior again approaches that of normal wool.

From the above facts one might be led to conclude that progressive increase in the degree of cross-linkage would result always in a steady

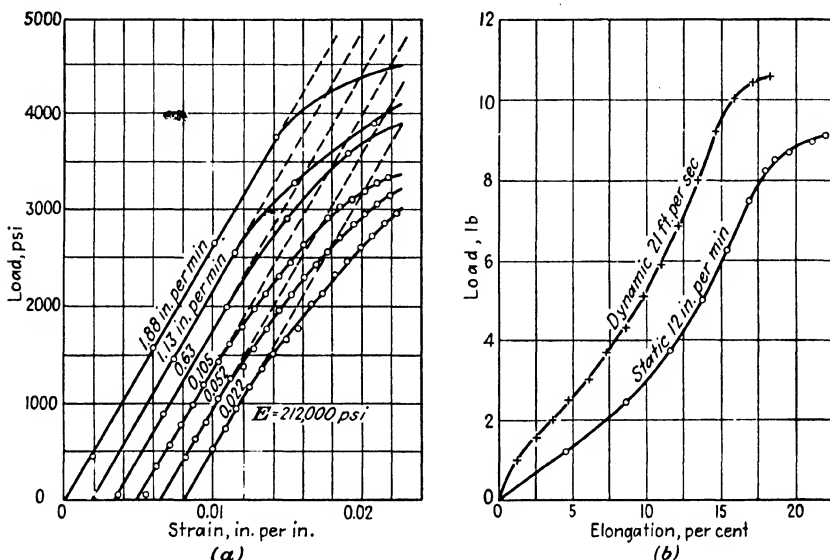


FIG. 9-6. Effect of rate of loading on tensile behavior of high polymers. (a) Cellulose acetate plastic, 26 per cent plasticizer. [W. N. Findley, *Proc. Am. Soc. Testing Materials*, **41**, 1231 (1941).] (b) Nylon fiber. [H. D. Smith, *Proc. Am. Soc. Testing Materials*, **44**, 543 (1944).]

increase in ultimate tensile strength, but experiments show that, in certain systems, increasing degrees of cross-linkage result first in a rise and later in a decrease. For example, methyl methacrylate copolymerized and cross-linked with a substantial fraction of diglycol methacrylate may have half the tensile strength of polymethyl methacrylate itself. This effect may be explained as follows: A small number of cross-links prevents molecular slippage when tension is applied but does not seriously interfere with the straightening of the chain molecules since the local consistency and internal Brownian motions of the chain sections will not be seriously hindered. Consequently, when the mass is stretched, the chains align and a relatively large number of them participate in bearing the externally applied stress; the tensile strength will be high because three factors are working in the same direction, *viz.*, (1) the reinforcing action of the cross-links; (2) the reinforcing action attributable

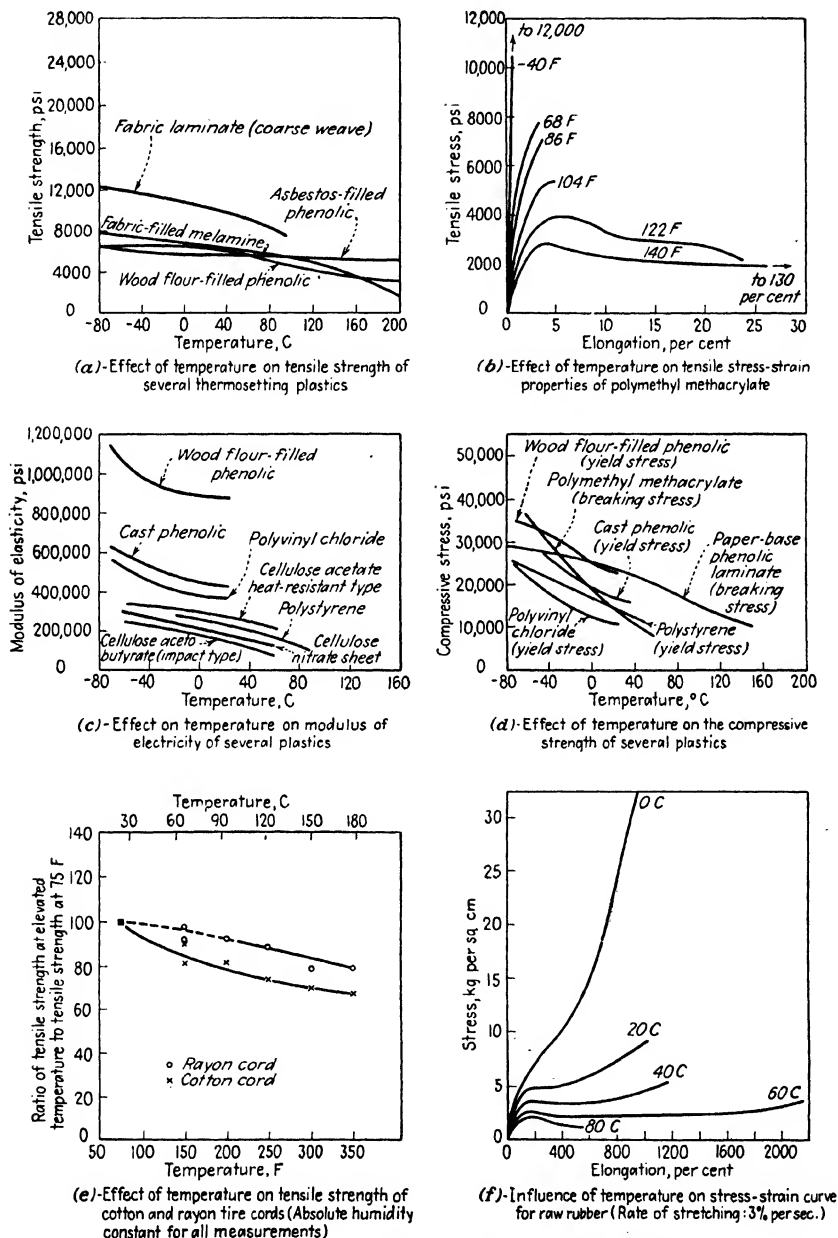


FIG. 9-7. Effect of temperature on mechanical properties of high polymers. [(a), (b), (c), (d) T. S. Carswell and H. K. Nason, in "Symposium on Plastics," Am. Soc. Testing Materials, 1944. (e) W. F. Busse, et al., *J. Applied Phys.*, 13, 715 (1942). (f) V. P. Rosbaud and E. Schmid, *Z. tech. Physik*, 9, 98 (1928).]

to chain alignment and closer packing under tension; (3) the participation of a large number of (straightened) chains or other structural elements in resisting the stress.

On the other hand, a *high* degree of cross-linkage always results in a high consistency and may lead to low ultimate tensile strength because of a serious interference with chain alignment and uniform load distribution. In other words, although factor 1 above is increased, factors 2 and 3 are reduced (see Secs. 1227 and 1306).

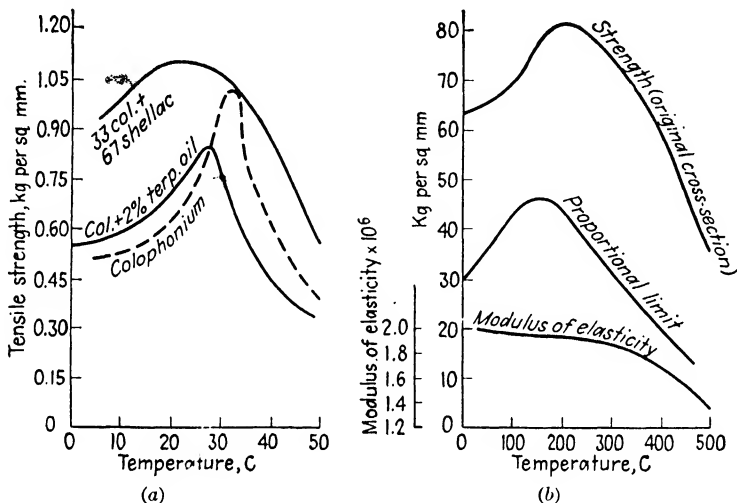


FIG. 9-8. Effect of temperature on tensile properties. (a) Rosin (colophonium) in some mixtures. (b) Carbon steel. (R. Houwink, "Elasticity, Plasticity, and Structure of Matter," 1940. By permission of The Macmillan Company, publishers, and Cambridge University Press.)

910. Rate of Loading. In general, rapid rates of loading result in higher breaking strengths and elastic moduli. Indeed, the entire stress-strain curve is raised, but the elongation at break may increase or decrease. Typical effects are shown in Fig. 9-6 and Table 7-4, p. 274. As stated in sections dealing with relaxation time and the rheological behavior of polymers, the rapid application of stress permits less relaxation and flow. Consequently, elastic behavior predominates. In general, the more plastic the material, the greater will be the effect of loading.

911. Temperature. As might be expected, elastic modulus, yield value, and tensile strength usually decrease with increase in temperature (Fig. 9-7). However, various cases are known of both crystalline and amorphous substances where the tensile strength first increases with temperature and only later decreases (Fig. 9-8). This apparent anomaly is explained on the same basis as the similar phenomenon occurring when external plasticizers are added (Sec. 908); *i.e.*, increased mobility of

structural units results in relief of localized internal stresses and also in the more even distribution of load over the cross section.

912. Comment. It is hoped that the discussion of the factors affecting the tensile strength has duly impressed the reader with the complexity of such a mechanical property. Other mechanical properties will not be treated in this extensive fashion though they are just as complex.

One should no longer be surprised by the widely differing strength values quoted in the literature for high-polymer materials. Like any rapidly developing field, this one is suffering from growing pains. Only lately have efforts to standardize methods of test and specifications begun to bear fruit. In this regard, the activities of the A.S.T.M. have been particularly noteworthy.

STATIC STRUCTURAL CONSIDERATIONS

913. A structural material must be capable of withstanding considerable stress over long periods of time without serious loss of shape or dimensions. In such a material, high yield value and elastic moduli are basic attributes, but these are by no means the only factors to be considered.

914. Strength Balance. A highly desirable feature in a structural material is good "strength balance"; *i.e.*, the strengths in tension, compression, and shear should be of the same order. Such strength balance widens the number of structural applications and minimizes the danger of structural failures. It is a matter of engineering experience that failures in performance are often traceable to low strength in one direction. For example, a member may be designed to withstand stresses in tension and then fail through being low in shear because through some unforeseen circumstance the member becomes subjected to shear stresses larger than it was intended or expected to encounter.

A high-polymer mass in which chain molecules or crystallites are preferentially aligned along one axis is a highly unbalanced material. Its tensile strength along the main axis is far in excess of that at right angles to this axis. This is characteristic of all fibrous materials. For example, the lack of strength balance in wood is shown by the aircraft spruce of Table 9-9 (compare tensile, compressive, and shear strengths). By contrast, the strength balance of typical structural metals is good. Mica, a plane-polymerized silicate, is strong along two axes but weak along the third so that it splits readily into sheets. It too lacks strength balance.

Materials in which there is a random arrangement of crystallites or total molecular disorder are more balanced in strength; and it follows that the arrangement and interbonding of molecules, on the one hand,

TABLE 9-9. STATIC STRENGTH PROPERTIES OF VARIOUS MATERIALS^a

Material	Specific gravity	Elastic modulus in tension, $\text{psi} \times 10^{-4}$ E_t	Elastic modulus in compression, $\text{psi} \times 10^{-4}$ E_c	Shear modulus, $\text{psi} \times 10^{-4}$ G	Tensile strength, psi σ_t	Compressive strength, psi σ_c	Shear strength, psi σ_s	Specific strengths, psi			Figures of merit in tension, $\text{psi} \times 10^{-4}$			Figures of merit in compression, $\text{psi} \times 10^{-4}$			Figures of merit in shear, $\text{psi} \times 10^{-4}$		
								Tensile σ_t/ρ	Compressive σ_c/ρ	Shear σ_s/ρ	E_t/ρ	E_c/ρ	G/ρ	E_t/ρ	E_c/ρ	G/ρ	E_t/ρ	E_c/ρ	G/ρ
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	(13)	(14)	(15)	(16)	(17)	(18)	(19)	(20)
1 Stainless steel 18-8, high tensile	7.90	29	29	11	185,000	150,000 ^b	100,000	23,400	19,000	12,700	3.67	0.464	0.059	0.367	0.464	0.059	1.39	0.176	0.022
2 Structural steel SAE 1020	7.85	29	29	12	65,000	45,000	45,000	8,300	5,700	5,700	3.69	0.471	0.060	0.369	0.471	0.060	1.53	0.194	0.025
3 Aluminum alloy 2024-T	2.75	10.3	10.3	3.8	68,000	44,000 ^c	41,000	24,700	16,000	14,900	3.74	1.36	0.495	3.74	1.36	0.495	1.38	0.502	0.183
4 Magnesium alloy AM-585	1.80	6.5	6.5	2.4	46,000	35,000 ^c	22,000	25,500	19,500	12,200	3.61	2.00	1.11	3.61	2.00	1.11	1.33	0.740	0.411
5 Laminated plastic; allyl resin CR 39B4, with Fiberglas fabric laminations crossed at 90 deg	1.85	3.1	2.2	53,400	42,500 ^d	22,500	28,800	23,000	12,200	1.88	0.905	0.490	1.19	0.643	0.347
6 Flax; single fibers	1.50	6.6 ^f	120,000	80,000	4.40	2.93	1.95
7 Paper; phenol-aldehyde with parallel paper laminations. Army Air Specification, 12036	1.35	2.6	1.4	0.3	28,000 ^h	19,000 ^h	3,000	20,700 ^h	14,100 ^h	2,200	1.92	1.43	1.06	1.04	0.768	0.568	0.222	0.164	0.122
8 Laminated plastic; phenol-aldehyde with fine-weave fabric laminations. Navy Specification, 17-P-5, type FBG	1.35	1.0	0.61	13,000 ^h	35,000 ^h	9,600 ^h	26,000 ^h	0.74	0.548	0.406	0.45	0.325	0.248
9 Compress, phenol-aldehyde with parallel laminated 1/8-in. spruce veneers	1.32	4.8	4.8	42,000 ^h	24,000 ^h	5,000 ^h	31,800 ^h	18,200 ^h	3,800 ^h	3.64	2.75	2.09	3.64	2.75	2.09
10 Phenol-formaldehyde thermoset; no filler	1.28	0.8	7,500	28,000	12,000	5,800	21,800	9,400	0.62	0.488	0.381	0.17	0.144	0.122
11 Polymethyl methacrylate	1.18	0.3	0.2	7,000	11,000	7,000	5,900	9,300	5,900	0.25	0.215	0.168	0.17	0.144	0.122
12 Polystyrene; no filler	1.06	0.2	0.4	6,000	15,000	6,500	5,700	14,100	6,100	0.19	0.178	0.168	0.38	0.156	0.336
13 Polystyrene, expanded	0.032	0.0011	40	20	20	1,250	625	625	3.02	7.03	16.3	3.02	7.03	16.3	1.07	33.5
14 Aircraft spruce	0.43	1.3	1.3	0.6	10,000	5,000	1,000	23,200	11,600	2,300	3.02	7.03	16.3	3.02	7.03	16.3	1.40	3.24	7.55
15 Balsa wood	0.13	0.37	0.37	1,500	1,500	1,500	23,200	11,600	2,300	2.84	21.9	168	2.84	21.9	168

^a Data from several sources, notably
 HOTT, S. L., "Metals and Alloys Data Book," Reinhold Publishing Corporation, New York, 1943.
 PLASTICS MATERIALS MANUFACTURERS' ASSOCIATION, "Technical Data on Plastics," Washington, 1945.

^b Yield point in compression.

^c Yield point in tension. Practically the same as yield point in compression for wrought alloys.

^d Crosswise.

^e Edgewise.

^f Flat.

^g Johnson single-shear method. Perpendicular to plies.

^h Lengthwise.

ⁱ Average stiffness.

and of larger units such as crystallites, fibrils, fibers, granules, and grains on the other, influence not only the strengths but also the strength balance of any real mass.

The desire to attain better strength balance is responsible for some highly important manipulative procedures. For example, in the manufacture of plywoods, native wood is cut into veneers, which are then laid up with the grain of alternate veneers at right angles to one another and glued together. One of the main reasons for doing this is to obtain better strength balance (Table 9-10). Again, synthetic thermosetting binders

TABLE 9-10. EFFECT OF CROSSING VENEERS ON THE STRENGTH BALANCE OF A PHENOLIC-RESIN-BONDED COMPREG

Material	Direction of test referred to grain of wood in outermost veneers	Specific gravity	Tensile strength, psi	Young's modulus, $\text{psi} \times 10^{-6}$
All veneers arranged with grain running in same direction.	Along	1.35	48,000	4.2
	Across	1.35	2,400	0.6
Alternate veneers crossed at 90 deg to each other.	Along	1.32	26,600	2.4
	Across	1.32	15,000	2.1

KUTCH, W., *J. Roy. Aeronaut. Soc.*, **44**, 44 (1940).

such as the phenolic and urea resins have low tensile and impact but high compressive strengths (Appendix C), whereas cellulosic and glass cloths possess the high tensile and impact strengths inherent in fibrous masses but lack the ability to resist compression; but by setting layers of the cloth in a continuous matrix of the thermosetting binder a material combining the good features of both binder and filler is obtained. The above are just two examples out of the hundreds of plastic-fiber, plastic-metal, rubber-fabric, rubber-metal, and metal-fiber combinations that are used in modern industry.

915. Instability. A short, squat compression block of cross-sectional area A made from a material having a compressive strength s_c will bear a compressive load equal to $s_c A$.

A tall, slender column is called an *Euler column*. If such a member is subjected to an axial compressive load, the slightest maldistribution or misalignment of the load sets up a bending moment that causes the column to deflect laterally (Fig. 9-9). Once the lateral deflection y has been established, on the inside of the curve there is superimposed on the compressive load P an added compression due to the bending moment Py . By contrast, the outside of the member is subjected to a tension. Bending, once started, tends to be self-aggravating; and if the load P is too

great, the column will fail by buckling. If, therefore, an Euler column of solid cross-sectional area A is built of a material having a compressive strength s_c , owing to the *instability* of the column just described, no such load as the theoretical $s_c A$ will be successfully resisted. The critical load

P_c is given by Euler functions, which have the general form

$$P_c = \frac{KEI}{l^2}$$

where P_c is the critical load, K a numerical constant, E the elastic modulus, I the moment of inertia, and l the length of the column. Under the load P_c given by the Euler formula the column is in neutral equilibrium. If the load is less than P_c , any lateral deflection will disappear when the load is removed. At loads greater than P_c a lateral deflection, once started, will increase rapidly, and failure by buckling will result.

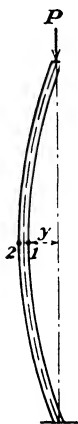


FIG. 9-9. Lateral deflection of a long compression member.

Instability of the kind described is encountered in any structural part that is thin or small in one or two dimensions.

916. Specific Strengths: Strength-Weight Ratios. On an equal volume basis, steel is stronger than dural, which, in turn, is stronger than wood (Table 9-9, columns 6, 7, 8). On this basis, organic high polymers cannot usually compete with metals as structural materials. However, there are many structures in which both strength and weight are important. Examples are furniture, automobile and truck bodies, and, of course, airplanes and gliders. The strength-weight ratio or specific strength of a material is defined as its strength divided by its gravity. Organic high polymers have low densities and, on an equal weight basis, their strengths fall more into line with those of metals. Thus, compare stainless steel and aircraft spruce in column (9) of Table 9-9.

917. Modulus-Weight Ratios. Assuming that a number of different materials are available for constructing the beams, columns, plates, or other members of a structure that must be both light and strong, how may the material with the best mechanical properties be chosen? What one requires to answer this question is a number or factor, readily calculated, that will permit direct quantitative evaluation of the materials in question. Such a number would be a *figure of merit*. It will now be shown that, although specific strengths are not usually sufficient to the purpose, suitable figures of merit can nevertheless be established in the form of modulus-weight ratios.

918. Axial Deflection of Stable Members. Short, thick compression members are relatively free from instability. Assume that a stable column of a given length is to be designed to withstand a compressive load, that different materials are available for the purpose, and that they will be used on an equal-weight basis.

Let P be the load, A the cross-sectional area, l the length of the column, E the elastic modulus in compression, and Δ the deflection produced by the load. For structural purposes the material will, of course, be stressed well within the proportional limit. Then, according to Hooke's law [Eq. (7-1)],

$$s = E\epsilon \quad \text{or} \quad \frac{P}{A} = E \frac{\Delta}{l}$$

from which

$$\Delta = \frac{Pl}{AE}$$

Since P and l are constants of load and design, $\Delta \propto 1/AE$. If the weight of material used for the member is a constant, $A \propto 1/\rho$ and

$$\Delta \propto \frac{\rho}{E} \quad (9-5)$$

Equation (9-5) states that the deflection produced in the column by the load is proportional to the ratio ρ/E . For a strong material the deflection will be small; for a weaker material it will be larger.

The derivation may be approached from a different angle. Instead of applying a constant load P , the deflection Δ may be established as a constant, *i.e.*, a maximum permissible deflection. If this is done

$$P = \frac{AE\Delta}{l} \quad \text{and} \quad P \propto AE$$

If the competing materials are compared on an equal-weight basis as before, $A \propto 1/\rho$ and

$$P \propto \frac{E}{\rho} \quad (9-6)$$

The important point is that this figure of merit is merely the reciprocal of that previously derived. Equation (9-6) states that on an equal-weight basis the material for which E/ρ is larger can carry a greater load within a permissible deflection. The figure of merit can be used in either form for comparison purposes. Since both E and ρ are readily obtained from handbooks, their ratio is a very easily applied figure of merit and, of two competitive structural materials, that for which the modulus-weight ratio is higher is the better. From columns (12) and (15) of Table 9-9 it

follows that, on an equal-weight basis, steel, dural, and aircraft spruce are about equally efficient for designing the type of member under consideration in spite of the large differences in column (3).

919. Bending Deflection in Beams. For beams, the design formula is

$$\Delta = \frac{KM}{EI}$$

where K is a constant dependent on load and size and M the bending moment.

It can be shown by similar treatment that, for this type of member, the figure of merit in terms of load-bearing ability is again E/ρ .

920. Deflections of Euler Columns and Other Thin, Unstable Compression Members. For an Euler column of fixed length and weight and of symmetrical cross section, it can be shown that $I \propto 1/\rho^2$ and that

$$P \propto \frac{E}{\rho^2} \quad (9-7)$$

Since the second power of the specific gravity appears in this figure of merit, light materials are likely to show to advantage. Referring to column (16) of Table 9-9, it will be seen that, whereas, on an equal-weight basis, for beam design steel and aircraft spruce are equivalent, the wood is about 15 times as efficient as the steel for Euler columns.

921. Plate Rigidity. Thin sheets or plates do not resist loads normal to their surface very well. As for beams, the structural-design formula is again $\Delta = KM/EI$, but in this case $I = at^3/12$, where a is the sheet width and t is its thickness. For plates of equal area and equal weights, $I \propto 1/\rho^3$, and

$$P \propto \frac{E}{\rho^3} \quad (9-8)$$

In this case, low-density materials exhibit an enormous advantage over those of high density when used on an equal-weight basis [columns (14) and (17), Table 9-9].

922. Torsional Deflections. Figures of merit for resistance to shear are calculated in similar fashion and prove to be the modulus of shear G divided by some power of the specific gravity (ranging from first to third power). Values are given in Table 9-9, columns (18) to (20).

923. Summary. Where materials are to be used on an equal-weight basis and stressed within the proportional limit, we may summarize as follows:

1. The relative efficiency of a structural material is given by its modulus divided by some power of its specific gravity.

2. The "strength" of a structural material depends on the type of member for which it is to be used. This point is emphasized in Table 9-11.

3. The figure of merit in any case has significance only if it is derived from the proper design formula and the materials are used within their elastic or proportional limits.

4. Where the second or third power of the specific gravity enters the figure of merit, light materials exhibit startlingly high relative efficiencies. In these cases, organic high-polymeric materials show to advantage.

TABLE 9-11. COMPARATIVE STRUCTURAL EFFICIENCIES ON THE BASIS OF STATIC FIGURES OF MERIT*

Material (see Table 9-9)	Applications where E/ρ is figure of merit, <i>e.g.</i> , axial and bending deflection	Applications where E/ρ^2 is figure of merit, <i>e.g.</i> , buckling of Euler columns	Applications where E/ρ^3 is figure of merit, <i>e.g.</i> , deflection of flat plates under loads normal to the surface
Load-carrying Efficiency for Equal Weights of Material			
Aircraft spruce.....	0.81	5.16	32.90
Compreg, spruce.....	0.98	2.02	4.21
Magnesium alloy....	0.97	1.47	2.24
Dural 24S-T.....	1.00	1.00	1.00
Steel, SAE 1020.....	0.99	0.35	0.12
Weight Efficiency for Equal Load-carrying Ability			
Aircraft spruce.....	0.81	2.27	3.21
Compreg, spruce.....	0.98	1.42	1.62
Magnesium alloy....	0.97	1.21	1.31
Dural 24S-T.....	1.00	1.00	1.00
Steel, SAE 1020.....	0.99	0.59	0.49
Weight of Material Required to Carry Same Load as Dural Member of Unit Weight			
Aircraft spruce.....	1.23	0.44	0.31
Compreg, spruce.....	1.02	0.70	0.62
Magnesium alloy....	1.03	0.83	0.76
Dural 24S-T.....	1.00	1.00	1.00
Steel, SAE 1020.....	1.01	1.70	2.04

* Efficiency of Dural 24S-T taken as unity in all cases.

For Dural 24S-T: $E_s = 10.3$, $\rho = 2.75$, $E_s/\rho = 3.74$, $E_s/\rho^2 = 1.36$, $E_s/\rho^3 = 0.495$.

The specific gravity and elastic moduli of a metal are stubbornly constant properties that remain virtually unaltered by cold working or heat-treatment. By contrast, as will be shown later in this chapter, it

is possible to vary these properties in plastic products over rather wide limits so that their figures of merit may be changed to suit various structural purposes.

THE MECHANICAL BEHAVIOR OF EXPANDED MATERIALS

924. From the previous sections it is evident that figures of merit for a structural material are often derived from design formulas which involve the moment of inertia of the cross section of the member. Strength formulas also often contain the value of the stress in the extreme fibers of the specimen, *i.e.*, the stress in the fibers or material faces farthest distant from the neutral axis. A case in point is the well-known flexure formula

$$M = s \frac{I}{c} \quad (9-9)$$

where M is the bending moment, s the stress in the extreme fiber, I the moment of inertia, and c the distance from neutral axis to extreme fiber.

Obviously, the resistance to external stress is not merely a matter of the intrinsic strength of the material of construction but also depends on the shape or form of the structural member. When materials are used on an equal-weight basis, members made of light substances have larger cross-sectional areas and, as previously seen in Secs. 920 *ff.*, the form factors under discussion operate in such a way that light materials possess superior figures of merit when the second or third power of the specific gravity enters the design formula.

The above factors often work to advantage when a material is naturally or artificially expanded (Sec. 853). For example, various native woods represent wood substance that has been expanded to different degrees by different botanical species in their growth processes. Thus, balsa has an apparent gravity of about 0.1, and the pore space is over 90 per cent of the total volume. By contrast, for blackwood, a dense species, the apparent gravity is about 1.0, and the pore space is about 30 per cent. Furthermore, the modulus of elasticity in compression for wood is given by the expression $k\rho$ (Table 9-15), where k is a constant and ρ the specific gravity. Hence the modulus for balsa is about $0.1k$, while that for the less highly expanded blackwood is $1.0 \times k$. The comparative figures of merit of wood substance expanded to these two different extents are therefore presumably as follows:

Wood	E	ρ	E/ρ	E/ρ^2	E/ρ^3
Balsa wood	$0.1k$	0.1	k	$10k$	$100k$
Blackwood	k	1.0	k	k	k

Similar trends are shown in the figures of merit of other rigid expanded materials, both natural and artificial, *e.g.*, cellular polystyrene and cellular vulcanized rubber. While no hundredfold increase in the figure of merit such as is shown above may result, nevertheless expansion tends toward enormous increases in equal-weight efficiencies (items 12 to 15, Table 9-9).

As a given material is expanded, its strength per unit cross section and its hardness decrease, for obvious reasons. Expanded materials are often used in so-called "sandwich" constructions. An expanded material is used as the core and is faced on both sides with sheets of stronger, denser, harder material. In this way the best features of both are utilized. The over-all figures of merit of the sandwich are high. The dense material is on the outside, where it is most effective in increasing the moment of inertia and where it is most needed because it has the hardness requisite for resisting denting, etc. The expanded core, besides affording lightweight construction, may also serve as thermal or electrical insulation, fireproofing, etc.

CREEP AND TIME-TO-RUPTURE VALUES

925. The evaluation of structural materials from simple static-strength data is not always adequate even for designing members for static structures. Static-strength data are obtained from standard tests in which the load is applied at a rate sufficient to break the test specimen in a matter of a few minutes. These methods do not take into account the elements of time, relaxation, and creep. Thus, the steel required for an edifice that may be planned to stand for a century is tested for breaking strength in a few minutes. As explained in Secs. 706 *ff.*, if the load is maintained long enough, a member will fail even at stresses well within its short-time breaking strength. The damaging effects of creep are, in general, two.

1. It results in a continually increasing deformation, which may eventually exceed permissible tolerances and thus render a machine or structural part inoperative.

2. A member tends to become unstable and weak with excessive deformation and may, as a result of creep, fail by buckling or at stresses far below the short-time breaking strength.

On the other hand, creep, if not too extensive, may be beneficial in that, if it occurs at points of highly localized stress, it may relieve such stress, equalize the load distribution, and actually delay or prevent failure.

The implications of creep are far-reaching. A stressed structural part may be designed with maximum efficiency only when the working temperature, creep rate, and expected life are known, along with the working stress.

926. General Aspects of Creep. Creep is usually studied by applying a constant tensile load at constant temperature and measuring the increase of elongation with time by means of a sensitive mechanical-optical or electrical-resistance strain gauge. In other words, the ordinary creep curve is a tensile-flow curve.

As indicated in Sec. 724, creep is composed of two parts; a retarded elastic deformation, which is called *primary creep*, and a nonrecoverable flow, termed *secondary creep*. The creep curve of a phenoplast is shown

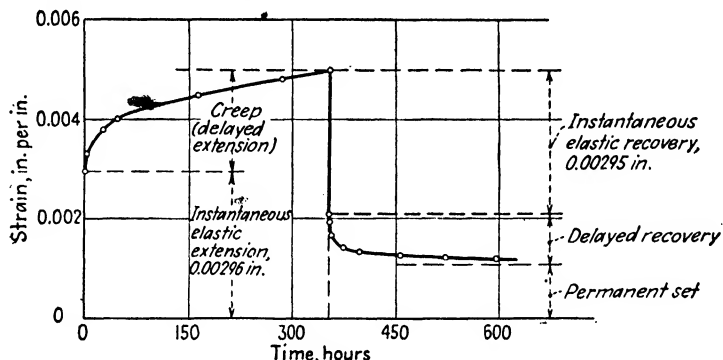


FIG. 9-10. Strain-time curve for cord-filled phenol-formaldehyde resin; stress 3,300 psi for 350 hr, 25 C, 50 per cent relative humidity. [D. Telfair, T. S. Carswell, and H. K. Nason, *Modern Plastics*, **21**, 137 (February, 1944).]

in Fig. 9-10. From molecular theory one would expect that strong primary or secondary valence forces, cross-linkage, and a high degree of crystallinity would tend to minimize creep. This is borne out in fact. Whereas at room temperature and low stress the creep of steels and many other high-modulus structural metals is so small as to be practically unmeasurable, that of organic high polymers is extensive, thermoplasts showing far more than mutaplasts (Fig. 9-11 and Table 9-12). *The relatively high creep rates of organic high polymers at atmospheric temperatures constitute their most serious limitation for many structural applications.*

In structural metals the primary creep is small compared with the instantaneous elastic deformation—of the order of 3 per cent. By contrast, organic high polymers exhibit a large amount of delayed deformation. In elastomers the instantaneous elastic deformation is only a small part of the total deformation.

927. Forms of Creep Curve. The creep curves of different materials vary considerably in form (Fig. 9-12). Curves of types A and B are prevalent for metals. Curve A is often met in organic high polymers. The apparently anomalous curve of type C has been encountered in thermosetting phenolic resins. These resins shrink after molding owing to slow progressive polymerization. At elevated temperature and low

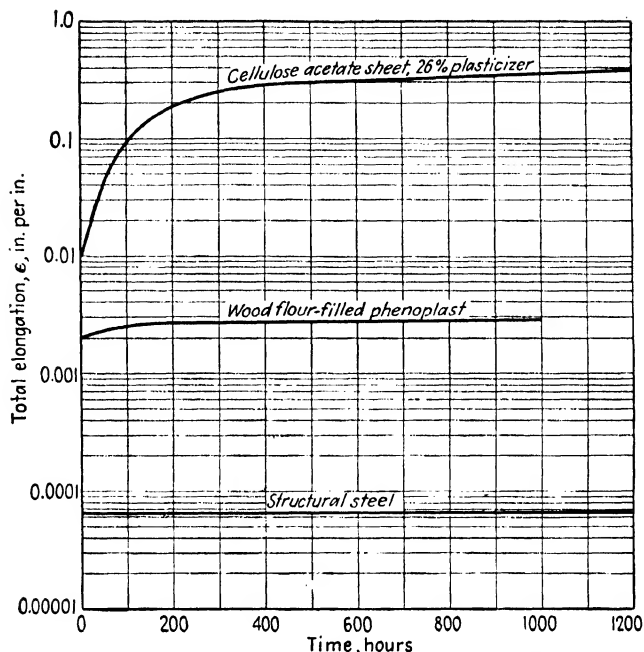


FIG. 9-11. Tensile-creep relations of various materials; stress 2,000 psi, 25 C, relative humidity 50 per cent.

stress this shrinkage proceeds at a faster rate than the elongation attributable to creep, accounting for the unusual curve. If the shrinkage rate is separately determined by holding a reference test piece at the experimental temperature under zero load and an appropriate correction is made, the creep curve as it would be if shrinkage did not occur can be constructed. This curve ("effect of stress," Fig. 9-13) turns out to be of type A.

Except when shrinkage effects are large, there is a high initial creep rate followed by a decreasing rate [Eqs. (7-23) to (7-26), page 302 ff]. After long periods of time, the deformation curve may become a straight line expressible by

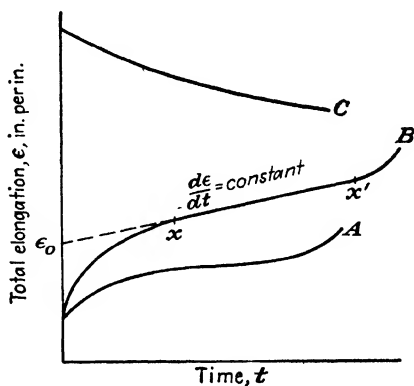


FIG. 9-12. Forms of creep curve at constant stress and temperature.

$$\epsilon = \epsilon_0 + \nu_0 t \quad (9-10)$$

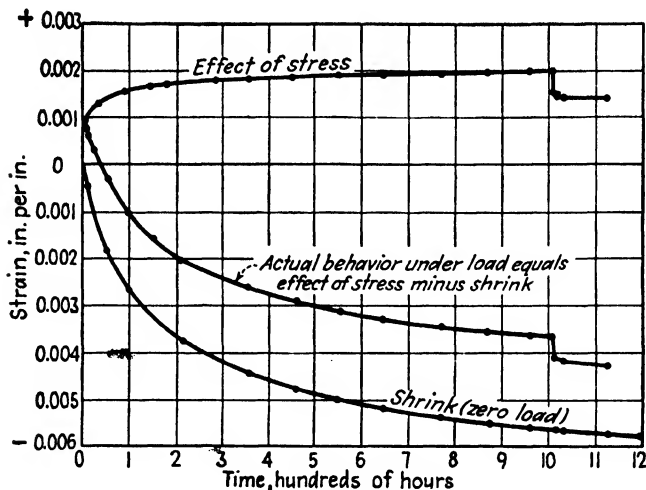


FIG. 9-13. Tensile-creep components of a wood-flour-filled phenolic; stress 488 psi, 194 F. [W. J. Gailus and D. Telfair, *Trans. Am. Soc. Mech. Engrs.*, **67**, 253 (1945).]

where ϵ is the total deformation, ϵ_0 the "initial strain," i.e., the intercept of the line of constant creep rate on the strain ordinate (Fig. 9-12), v_0 the minimum (constant) creep rate, and t the time.

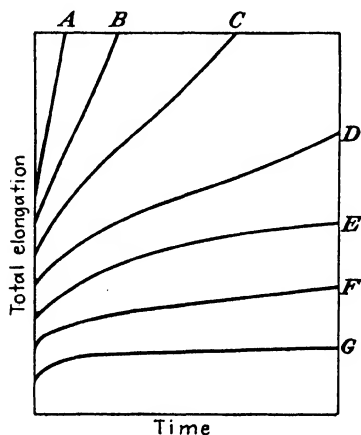


FIG. 9-14. Creep curves of a material at constant temperature and different stresses, or at constant stress and different temperatures. In first case A is curve at highest stress, G at lowest stress. In second case A is curve at highest temperature, G at lowest temperature.

928. Factors Affecting Creep of High Polymers. As one would expect from theory, the creep rate for any given material increases with rise in temperature and stress. The form of the creep curve also varies. For many metals and plastics the general behavior is as shown in Fig. 9-14.

The temperature coefficient of creep is very high, indicating an activated process (Sec. 727). This presents a major difficulty in creep testing since it means that precise control over temperature must be maintained for hundreds, thousands, or even millions of hours. For example, at around 1000 F a rise of 6 F may double the creep rate of

steel (forged, 0.39 per cent carbon). If a Bakelite beam is subjected to flexure at 120 C and the load is then released, the final deflection is reached

in a few seconds at 120 C.; but if it is cooled to room temperature before load release, the deformation is effectively "frozen in" and about 10,000 years is the calculated time required for the final deflection to be attained. At 70 C the creep of filled compression-molded phenoplasts is about three times as great as at room temperature.

The creep behavior of high polymers is generally less predictable than that of metals owing to complicating factors. For one thing, the creep rates of most high polymers are sensitive to humidity, the water vapor acting as plasticizer. This further complicates their testing in that it becomes essential to maintain rigid long-time control over both humidity and temperature. There is a trend toward standardizing on 25 C (77 F) and 50 per cent relative humidity as the conditions for basic creep testing of plastics. Other complications are the shrinkage due to after-polymerization, which is particularly noticeable in mutaplasts and can lead to the anomalous behavior typified by curve *C* of Fig. 9-12, and the change in composition of thermoplasts during creep testing due to the loss of plasticizer. Furthermore, particularly at elevated temperatures, many organic polymers are subject to chemical change, notably oxidation. For example, it has been shown that the creep and relaxation of rubber vulcanizates are intimately associated with oxidative chain rupture and cross-linkage (Sec. 1330). All these effects are strongly temperature dependent. Finally, it should be recalled that binder-filler combinations are nonhomogeneous and anisotropic, particularly laminates. These factors also complicate the rheological behavior.

929. Creep Data. Since creep testing is difficult and time-consuming, it is desirable to have methods for obtaining long-time data from relatively short tests. For metals it is often assumed that a constant minimum creep rate is eventually reached. On this assumption Eq. (9-10) is used to define the creep-time relation, and a set of so-called "McVetty diagrams" are constructed, from which extrapolations of total deformation for times as long as 20 years are made from relatively short-time tests.

The dangers involved in extrapolation are obvious. Referring to curve *B* of Fig. 9-12, the creep rate often changes with time; and unless the expected service life of a structural part falls in a region of constant creep such as xx' of the diagram, extrapolated values are invalid. Furthermore, large extrapolations are unsafe unless the time required to rupture the material at the stress in question is known. The only safe way to obtain complete and reliable creep data is to measure creep all the way to rupture of the specimen. From such measurements the creep rate, total strain at break, time to rupture, and maximum permissible long-time working stress are all established.

Of the empirical equations that have been proposed to describe the

creep of plastics, one of the most general is the power function

$$\epsilon = \epsilon_0 + mt^n \quad (9-11)$$

where m and n are constants. It will be seen that Eq. (9-10) is the special case of Eq. (9-11) for which n is unity. The factors ϵ_0 and m vary with the stress, whereas the power n is independent of it. Equation (9-11) may be written

$$\log(\epsilon - \epsilon_0) = \log m + n \log t \quad (9-12)$$

If $\log(\epsilon - \epsilon_0)$ is plotted against $\log t$, this is the equation of a straight line. The creep of many plastics appears to follow this equation fairly well (Fig. 9-15), but it needs more extensive confirmation.

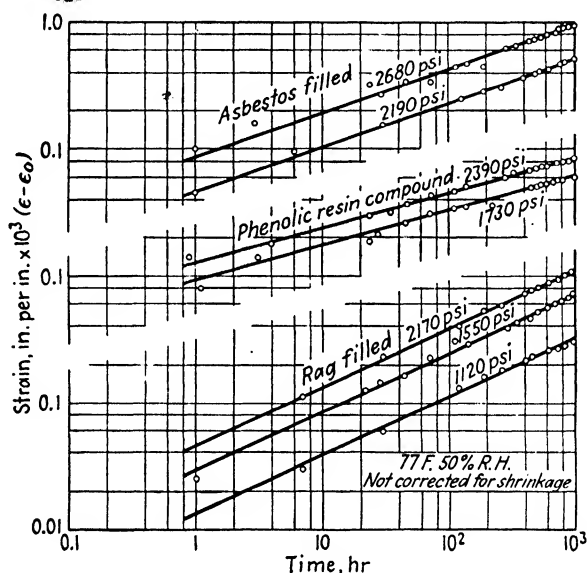


FIG. 9-15. Strain-time relationships for tension creep tests of three phenolics. (W. N. Findley, in "Symposium on Plastics," Am. Soc. Testing Materials, 1944.)

For comparing the characteristics of plastics, the trend is to test creep at various stresses at 77 F and 50 per cent relative humidity and emphasize the 1,000-hr data, *i.e.*, the stress required to cause rupture in 1,000 hr, and creep and total elongation in 1,000 hr under a stress of 2,000 psi. At the current writing, creep data on plastics are meager, and there is a great need for additional measurements. Some results are given in Table 9-12 and Fig. 9-16. From Table 9-12 it will be seen that the continuous tensile stress required to rupture the listed materials in 1,000 hr, a relatively short life for a stressed structural part, is roughly 40 to 70 per cent of the short-time tensile strength. There is, of course, a rough correlation between elastic modulus and creep deformation, the latter being low when

TABLE 9-12. TENSILE-CREEP DATA ON VARIOUS MATERIALS
(77 F, 50 per cent relative humidity)

Material	Static tensile properties			Creep data					Refer- ence
	Elastic modulus, psi $\times 10^{-6}$	Elonga- tion at break, %	Tensile strength, ps	Time-rupture strength		Total elongation at end of 1,000 hr at 2,000 psi (instanta- neous initial plus delayed deforma- tion), in./in.	Creep at end of 1,000 hr at 2,000 psi (total deformation minus instantaneous initial deformation), in./in.		
				Tensile load required to rupture specimen in 1,000 hr	% of static tensile strength				
Cellulose acetate sheet, 26 % plasticizer.....	0.212	38	4,700	2,430	52	3.45×10^{-1}	3.36×10^{-1}	1	
Polymethyl methacrylate, cast sheet.....	0.407	5	8,690	3,900	45	6.00×10^{-2} (stress of 2,475 psi)	2	
Phenol-formaldehyde molded plastics:									
100 % phenolic resin, thermoset, 0 % filler.....	0.85	1	8,900	2,000	23	2.8×10^{-2}	4.8×10^{-4}	3	
50 % resin, 50 % cotton cord.....	1.10	0.7	6,000	2,600	43	3.4×10^{-2}	1.53×10^{-3}	3	
50 % resin, 50 % wood flour.....	1.15	0.7	6,100	2,700	44	2.7×10^{-2}	0.93×10^{-3}	3	
50 % resin, 50 % chopped canvas.....	1.3	0.7	6,100	2,600	43	2.7×10^{-2}	1.12×10^{-3}	3	
40 % resin, 60 % asbestos.....	1.5	0.4	5,700	3,000	53	1.8×10^{-2}	4.3×10^{-4}	3	
50 % resin, 50 % mica.....	3.2	0.3	5,400	2,300	43	0.7×10^{-2}	1.0×10^{-4}	3	
Phenolic laminate, grade L. Fine-weave cotton- fabric laminations.....	1.45	2	16,520	11,000	67	2	
Phenolic laminate, grade XX. Paper lamina- tions; 50 % phenolic resin.....	1.70	1	16,540	11,000	67	2	
Phenolic laminate. 58 % Mitscherlich (sulfite) paper laminations, 42 % resin.....	2.27	0.7	19,600	8,500 (estimated)	43	1.22×10^{-2}	3.4×10^{-4}	1	
Aluminum 3S-1/2 H.....	10.3	16	21,000	3.14×10^{-4}	1.2×10^{-4}	4	
Steel SAE 1020.....	29	35	65,000	6.9×10^{-6}	Immeasurably small		

1 FINDLEY, W. N., in AMERICAN SOCIETY FOR TESTING MATERIALS, "Symposium on Plastics," Philadelphia, 1944.

2 CHASMAN, B., *Modern Plastics*, **21**, 145 (February, 1944).3 TELFAIR, D., T. S. CARSWELL, and K. NASON, *Modern Plastics*, **21**, 137 (February, 1944).4 MAMIN, J., and L. E. ZWISLER, *Proc. Am. Soc. Testing Materials*, **40**, 937 (1940).

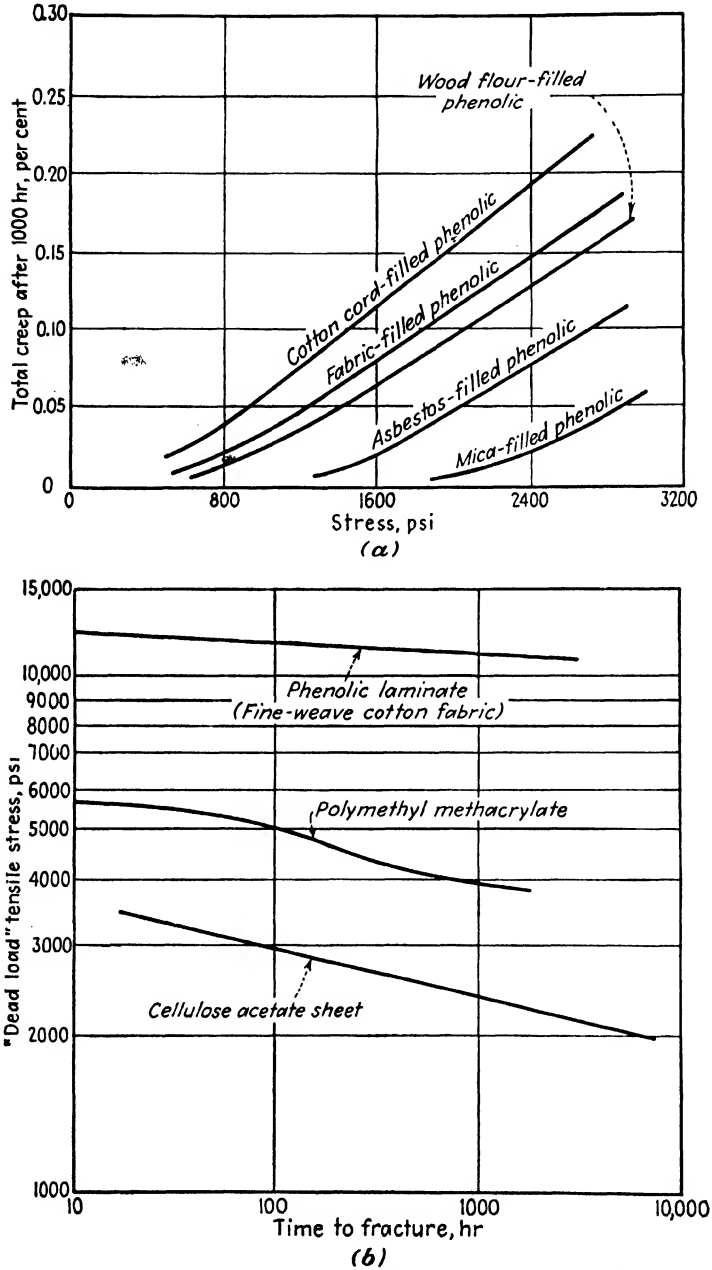


FIG. 9-16. Creep data for plastics at room temperature. (T. S. Carswell and H. K. Nason, in "Symposium on Plastics," Am. Soc. Testing Materials, 1944.)

the former is high. Fair degrees of correlation between creep, impact strength, and notch sensitivity also exist in the directions predicted by theory.

930. Minimizing Creep in Plastic Parts. The creep of organic high polymers at elevated temperatures is so great that it completely precludes their use per se as stressed members.

At room temperature, the creep of plastics of the thermoplast category is one to three orders of magnitude greater than that of mutaplasts, while the creep of mutaplasts is one to eight orders of magnitude greater than that of structural metals.

No plastic per se has sufficient creep resistance to serve as a highly stressed member. By combining thermosetting binders with suitable high-strength laminated fillers, it is possible to produce materials that can compete with metals at room temperature, provided that the unit stress is not too high or the expected life too long. This is particularly true if the materials are to be used on an equal-weight basis and the figure of merit involves the second or third power of the specific gravity.

After-shrinkage, warpage, and creep of themosets can be eliminated to a certain degree by thorough curing or after-baking.

It will be shown later in the chapter that both the elastic moduli and creep resistance of a binder-filler product depend upon the pressure at which the material is molded and can be considerably improved by choice of the optimum molding pressure.

Proper design and the use of metal inserts can very considerably overcome the deformation under stress in a "plastic" member. The method is fundamentally to minimize stress in the plastic portion of the part, mainly by using ribbed construction or including metal inserts to take the direct stress at a point and distribute it over a large area.

STRESS CONCENTRATION AND NOTCH EFFECTS

931. Some aspects of the flaw effect have been discussed in Secs. 712, 905, and 906. If from a given material one prepares two flexural test specimens of the dimensions shown in Fig. 9-17, one might expect them to break under the same load since presumably the same effective cross section is involved in resisting externally applied load. However, this is not the case; the notched specimen breaks under a smaller load than

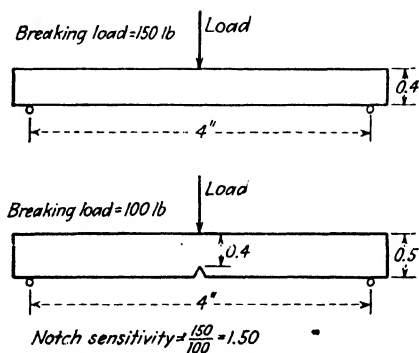


FIG. 9-17. Notch effect in flexure specimens.

the unnotched. The *notch sensitivity* of a material is defined as the ratio of the strength of an unnotched sample to that of a notched sample of equal depth behind the notch.

932. Stress Concentration around Notches. A notch results in high local stress concentration. Figure 9-18 shows the principal stresses at the surfaces of a notched bar that is subjected to bending. The upper part is in compression, the lower part in tension, as usual; but at the apex of the notch the tension stresses are several times larger than would exist if no notch were present. These cause the specimen to fail at lower breaking loads. Almost everyone is familiar with the fact that a piece of glass tubing breaks much more readily when a small surface notch is introduced by making a sharp scratch with a file.

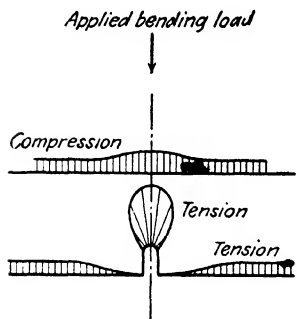


FIG. 9-18. Principal stresses at the surface of a notched bar under flexure.

The matter goes much further. Of a series of similar notches, say 45-deg V-shaped notches of equal-depth, that with the sharpest apex or the lowest radius of curvature causes the greatest local stress concentration and notch sensitivity. To return to our glass tubing, it is a matter of common experience that a dull file that yields a scratch with a rounded apex is not so effective for inducing break as a sharp file. In reporting notch sensitivity it is therefore essential to specify the exact nature of the notch.

It is also well known that materials differ radically in notch sensitivity. In ordinary glass it is extremely high, while in mild steels it is scarcely detectable. For plastic products Fig. 9-19 illustrates not only a wide divergence of notch sensitivity in flexure but also a marked difference in response of the latter to notch sharpness. The notch sensitivity of a material in flexure, tension, compression, and impact may vary considerably. In general, the more brittle a material, the greater its notch sensitivity and the greater also its response to notch sharpness.

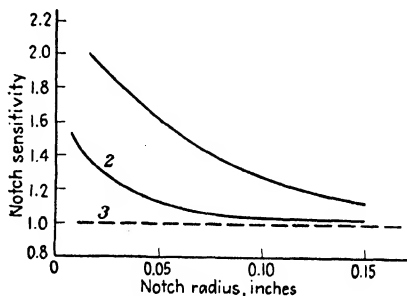


FIG. 9-19. Notch effect (approximate) in various plastic products. Curve 1: wood-flour-filled phenolic; cellulose-filled melamine; unfilled polymethyl methacrylate. Curve 2: flock-filled medium-impact phenolic; mica-filled phenolic. Curve 3: fabric-filled melamine; unfilled polystyrene. [H. M. Quackenbos, *Bakelite Review*, 18, 18 (July 1946).]

933. Design Considerations. Holes, threads, corners, or angles at changes in section may all be considered as notches, in every case resulting

in one or more points of high stress concentration (Fig. 9-20). The importance in respect to design and material selection is obvious. Consider two materials with flexural strengths of 12,000 and 9,000 psi, respectively. Assume the respective notch sensitivities for a notch radius of 0.010 in. to be 2.0 and 1.0. The effective flexural strengths in a member containing such a curvature will then tend to be $12,000/2$, or 6,000, psi for the first and $9,000/1$, or 9,000, psi for the second. Figure 9-20*d* shows

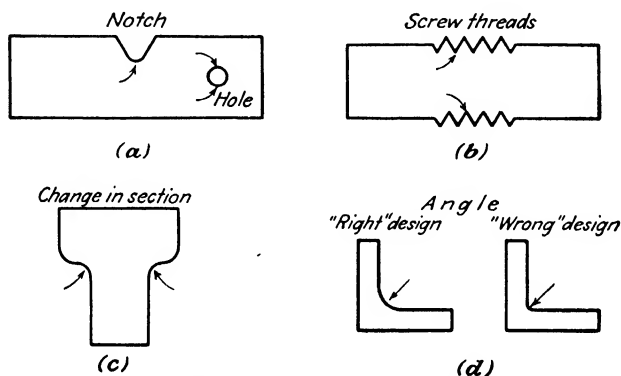


FIG. 9-20. Notch effect. Arrows indicate points of weakness.

a case of right and wrong design for a part made of notch-sensitive material.

Simple design rules may be stated as follows:

1. Avoid notches, corners, holes, angles, and changes in section whenever possible.
2. When such discontinuities must be present, (a) minimize the notch effect by making radii of curvature as large as possible; (b) use the materials of construction on the basis of nominal strength divided by the notch sensitivity for the radius employed.

At the current writing there is great need for more data on notch sensitivities. Only in impact testing has suitable attention been given to this factor.

934. The Behavior of Glass. Although strong in compression, glass is weak in tension. Furthermore, it is highly notch-sensitive. When it is subjected to bending as in Fig. 9-17, failure takes place rapidly, the break starting on the tension-stressed surface of the member. Relatively recently, notable improvements have been effected by two methods called *toughening* and *casing*. In toughening, the surfaces of the glass are thrown into a state of compression by sudden chilling. In casing, two thinner layers of glass with a lower coefficient of expansion are fused, or "flashed," to a thicker inner layer with a high coefficient of expansion. As the resulting sandwich cools, the glass of the inner layer contracts

more than that of the surface layers and therefore the latter are thrown into a state of compression exactly as in toughened glass.

When sheets of these improved glasses are subjected to bending, the normally induced tension of flexure is counteracted by the compression at the surfaces. Flexural strength may thus be increased fivefold. The glass may be bent or twisted to a marked degree. It is insensitive to sudden temperature changes and much more resistant to mechanical shock. As long as the compression layer is not penetrated, the notch sensitivity is much lower than that of ordinary glass. When the compression layer is punctured by a scratch or blow, the glass implodes and crumbles into small pieces far less dangerous than the large shards resulting when ordinary glass breaks. It may therefore be used as safety glass for windshields, etc. (see also Sec. 1022).

Brittle materials tend to be notch-sensitive, and it is well known that notch or flaw sensitivity is likely to be extreme in highly crystalline materials. Furthermore, it increases when load is applied at rapid rates. A theoretical explanation is offered in Sec. 949.

FACTORS AFFECTING PROPERTIES OF A BINDER-FILLER PRODUCT

935. Let us assume that it is desired to produce from a high-polymer binder and a filler a plastic product which will have a certain desired set of properties. What are the factors that must be considered? It turns out that there are five main determinants.

1. *The nature of the binder.* This determinant is quite obvious. If the chosen binder has high tensile strength, the final product will tend to have high tensile strength; if it is thermosetting, the finished product will tend to exhibit a relatively high creep resistance. In other words, the properties of the binder are imparted to the final product.

2. *The nature of the filler.* What has been said about the binder applies likewise to the filler. If the filler has high impact strength, the product will tend to exhibit high impact strength, etc. As pointed out in Sec. 802, the physical state of subdivision of a filler may exert far-reaching effects.

3. *The relative amounts of binder and filler.* This factor is not so obvious as one might at first think. The significant point here is that some properties of a binder-filler combination are linear functions of the percentage composition but others are not and may pass through a maximum. Figure 9-21 is illustrative. Needless to say, if it is desired to make the product of highest compressive strength from the binder-filler combination in question, the optimum percentage composition must be known. At present, this optimum can be determined only by trial. Reinforcing fillers for rubbers similarly exert a maximum effect at an

optimum concentration (Fig. 13-7, page 569). Creep characteristics also vary with the percentage composition (Table 9-13).

4. *The molding pressure.* It is an interesting and important fact that the creep characteristics, strengths, moduli, and densities (and hence the

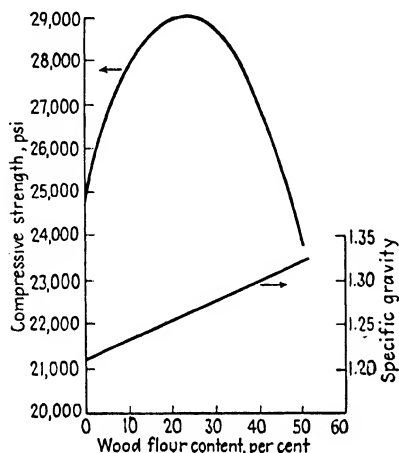


FIG. 9-21. Types of effects of fillers on properties of a binder-filler product; cresol-aldehyde binder and wood-flour filler. [N. A. de Bruyne, *J. Roy. Aeronaut. Soc.*, **41**, 523 (1937).]

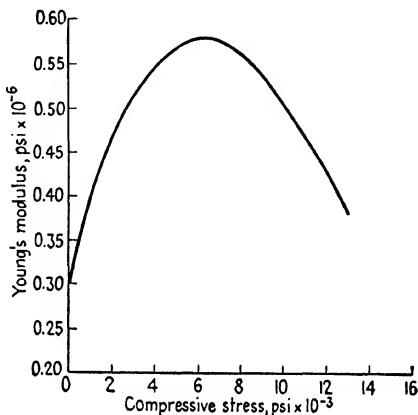


FIG. 9-22. Effect of pressure on Young's modulus of an unfilled thermoset cresol-aldehyde resin. [N. A. de Bruyne, *J. Roy. Aeronaut. Soc.*, **41**, 523 (1937).]

figures of merit) of high-polymer binder-filler systems are considerably modified by the pressure employed during molding. The variations are nonlinear, the curves either passing through a maximum or reaching a plateau (Fig. 9-22 and Table 9-13).

TABLE 9-13. EFFECT OF PERCENTAGE COMPOSITION AND MOLDING PRESSURE ON TENSILE STRENGTH AND TIME-RUPTURE STRENGTH

Material	Phenol-formaldehyde resin content, %	Molding pressure, psi	Tensile strength, psi	Time-rupture strength (tensile stress required to rupture in 1,000 hr), psi
High-strength paper laminated phenoplast.	9	2,850	20,000	10,200
	31	2,850	29,000	16,500
	44	2,850	28,000	14,900
High-strength paper laminated phenoplast.	31	950	27,800	13,300
	31	2,850	31,000	16,100
	31	8,550	31,000	17,200

As in the case of factor 3, there is at present no theoretical basis for calculating optimum molding pressures. They must be determined by trial.

5. *The molding temperature.* Both the molding temperature and the molding time (total application of heat) exert important effects on the strength characteristics of molded pieces. This is true for both thermoplasts and thermosets.

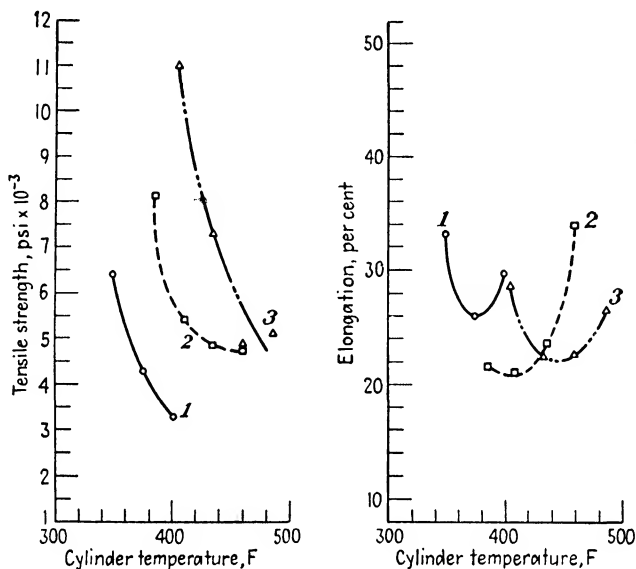


FIG. 9-23. Effect of molding-cylinder temperature on tensile properties of three cellulose acetate-butyrate mixes. [R. H. Ball, C. E. Leyes, and A. A. Melnychuk, *Ind. Eng. Chem.*, **37**, 240 (1945).]

With thermosetting mixes, if the temperature is too low or the time too short for the completion of sufficient cross-linkage, the pieces will be weak. For both thermoplastic and thermosetting mixes, too high a temperature or too prolonged heating usually results in inferior strengths due to decomposition or other chemical modification.

The far-reaching effects of molding temperature upon the mechanical properties of cellulose acetate-butyrate, a typical thermoplast, are shown in Fig. 9-23. In thermosets this "direct" heat effect is masked because increase in temperature usually influences the extent of cross-linkage, which, in turn, may produce either an increase or a decrease in tensile strength and other strength properties (Sec. 909).

A good example of the effect of molding temperature is afforded by vulcanized rubber (Fig. 13-4, page 561).

NATIVE WOOD

936. Composition. Wood is a complex mixture of substances (Table 9-14). In green wood, water may constitute one-third to two-thirds of

TABLE 9-14. AVERAGE COMPOSITION OF SPRUCE WOOD ON DRY BASIS

Item	Wt %
Cellulose.....	50
Lignin.....	30
Pentosans and other carbohydrates.....	16
Fats, waxes, terpenes, resins other than lignin, etc.....	4

the total weight. After it has been seasoned, moisture is present in amounts that vary in accordance with the humidity of the environment

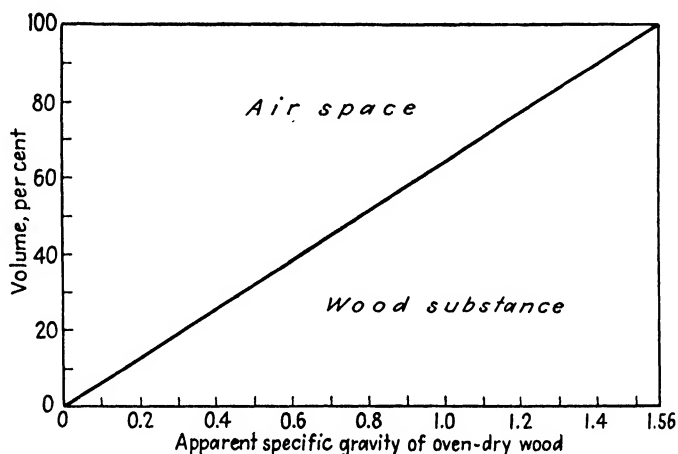


FIG. 9-24. Native woods as expanded materials:

Balsa.....	0.13	White ash.....	0.64
Cedars, white and red.....	0.32-0.35	Longleaf pine.....	0.64
White pine.....	0.37	Red oak.....	0.66
Black willow.....	0.41	Yellow birch.....	0.67
Yellow pine.....	0.42	Sugar maple.....	0.68
Firs and spruces.....	0.40-0.43	White oak.....	0.71
Hemlocks.....	0.43	Slash pine.....	0.76
Redwood.....	0.44	Blackwood.....	0.96
Cypress.....	0.48	Ironwood.....	1.08
White elm.....	0.55	Lignum vitae.....	1.3
Black gum.....	0.55	Lignostone.....	1.45

These are native United States woods with the following exceptions: balsa—tropical America; lignum vitae—West Indies; lignostone—a highly compressed wood product.

and may range between 0 in oven-dried to 30 per cent in completely humidified specimens.

Although different biological species vary rather widely in composition, the two main solid constituents are always cellulose fiber and the natural resin, lignin.

937. Structure. The true specific gravity of solid wood substance is practically the same for all botanical species and is about 1.56. However, the apparent gravities of all native woods are less than this. They are cellular, porous, naturally expanded materials. The amount of expansion varies enormously from one species to another, the apparent specific

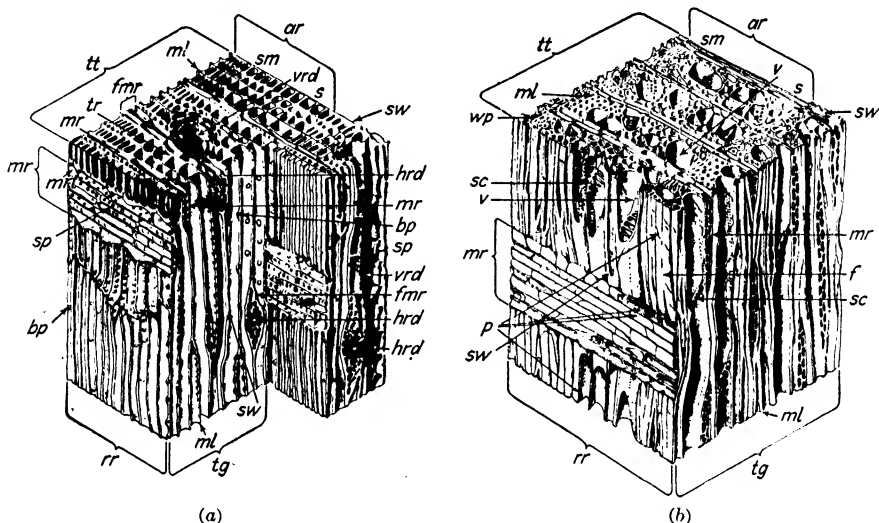


FIG. 9-25. Magnified blocks showing gross structure of wood. (a) Typical softwood. (b) Typical hardwood.

ar, annual growth ring; bp, bordered pit; f, fiber; fmr, fusiform wood ray; hrd, horizontal resin canal or duct; ml, middle lamella; mr, wood ray; mrt, wood ray tracheid; p, pit; rr, radial surface; s, springwood; sc, scalariform perforation between vessels; sm, summerwood; sp, simple pit; sw, secondary wall; tg, tangential surface; tr, tracheid; tt, transverse surface; v, vessel or pore; vr, vertical resin canal or duct; wp, wood parenchyma. [L. J. Markwardt, *Proc. Am. Soc. Testing Materials*, **43**, 435 (1943).]

gravities ranging from roughly 0.1 in balsa to as high as 1.3 in *lignum vitae*. The following relationship holds.

$$\text{Air space} = 1 - \frac{\rho}{1.56} \quad (9-13)$$

where ρ is the apparent specific gravity (Fig. 9-24).

Woods are divided into two main botanical groups, the *hardwoods*, or broad-leaved trees, and the *softwoods*, or conifers. The terms are misleading in that they do not properly refer to the actual hardness. Many hardwoods are softer than many softwoods.

Microscopy reveals that the gross structures of woods are extremely complex (Fig. 9-25). The basic unit of the gross structure is the cell, or fiber, which is a hollow tube with a central canal and a thick wall. For different species of softwoods the fibers range from 2 to 5 mm in length, while for hardwood species they run from 0.6 to 1.4 mm.

Most of the fibers are oriented along the grain of the wood. They are normally cemented together by lignin, which acts as a natural plastic binder, or matrix. In other words, native wood is a plastic binder-fibrous filler product. When the lignin is carefully removed by chemical means, it is possible to leave behind a continuous structural skeleton of the cellulosic fibers (Fig. 9-26).

Examination of the cross section of a tree trunk shows that the cells are nonuniform. Those formed during periods of rapid growth, *e.g.*, springwood, are comparatively large in cross section, thin-walled, and weak, while those formed when the tree is less active, *e.g.*, summerwood, are smaller and thicker walled. Hence summerwood is denser and stronger than springwood.

Scattered among the fibers of hardwoods are large continuous passages known as *pores* or *vessels*. Their size and distribution differ from one species to the next. Such pores are essentially absent from softwoods. Hence softwoods are in general more uniformly expanded than hardwoods.

Like other natural fibers, a wood fiber is built up of smaller morphological units. There is a thin primary wall, a thick secondary wall, and sometimes a tertiary layer, all containing fibrils arranged spirally and preferentially aligned with regard to the main fiber axis. Crystallites and amorphous regions exist in the fibrils, the former also oriented along the fibril main axis. In other words, in wood, structural organization goes further than in native cotton fibers (Sec. 525). As with the latter, cellulose molecules are aligned in crystallites, crystallites aligned in fibrils, and fibrils aligned in fibers. But in wood there are added features, (1) fibers aligned along a grain and (2) the setting of these aligned fibers in a matrix of the amorphous plastic binder, lignin.

In keeping with its structure, native wood is highly anisotropic. Along the grain its tensile strength is 20 to 40 times greater than across the grain. Although the matrix of lignin imparts to wood a rigidity and ability to withstand compression such as is not shown, for example, by a cotton rope, its compressive strength is nevertheless low as materials of construction go and it lacks strength balance (Table 9-9).



FIG. 9-26. Highly magnified cross section of wood fibers. The lignin, which cements the fibers together, has been chemically removed, leaving the hollow fibers appearing as separate units. The chemical pulping of wood in the paper-making industry is essentially a process of dissolving the lignin to separate the fibers. [L. J. Markwardt, *Proc. Am. Soc. Testing Materials*, **43**, 435 (1943).]

An integral part of the gross structure of wood is the various growth defects such as knots and pitch pockets. Wherever these massive flaws appear, the wood is very weak. To summarize, native wood is an expanded, highly anisotropic, and highly nonuniform material.

938. Swelling and Shrinking of Wood. When dry wood is exposed to a humid atmosphere, water is absorbed by the cellulose and the wood undergoes extensive swelling. The reaction is of the nonpermutoid type, solvation occurring only in the amorphous regions and at the crystallite surfaces (Sec. 434). Wood can absorb about 27 per cent of its own weight

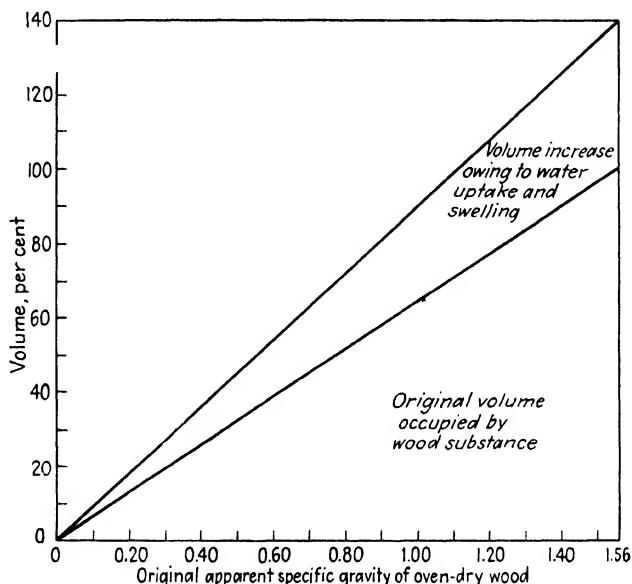


FIG. 9-27. Swelling of wood by moisture.

of water without any free unbound water being present. Since there is molecular, fibrillar, and fiber alignment along the grain, the swelling is anisotropic, taking place mainly at right angles to the grain.

If one starts with dry samples of various species of wood and humidifies them completely, the final increase in volume due to swelling is found to be directly proportional to the original apparent gravity. This is in accord with the fact that the water uptake is a function of the cellulose content; the more wood substance originally present per unit volume, the greater the degree of swelling. Hence, although dense woods may swell (and shrink) at a lower rate, they are inherently subject to larger total dimensional swelling changes than light woods. These facts are summarized in Fig. 9-27, which shows the very considerable dimensional changes that wood can undergo due to swelling by moisture.

The extent of solvation and swelling varies with the temperature and humidity of the environment. At 70 F and 60 per cent relative humidity the equilibrium moisture content is about 11 to 12 per cent. In a dry atmosphere part of the water of solvation is released, and the wood shrinks. In the normal course of events, therefore, native wood is continually undergoing cycles of expansion and contraction as the atmospheric environment changes. This can lead to the ultimate loosening or breakdown of joints, a very serious matter in wood construction. Furthermore, it means that wooden members or parts do not hold to dimension well. Finally, since the surface of a wood specimen swells or shrinks more rapidly than the interior, high internal stresses are set up, which often result in checking or splitting.

939. Effects of Moisture and Apparent Specific Gravity on Mechanical Properties. Moisture plasticizes cellulose. As the moisture content of wood increases, its strength decreases. For example, for Sitka spruce,

$$\text{Modulus of rupture} = 15,580 \times 10^{-0.016H} \text{ psi}$$

$$\text{Max. crushing strength parallel to grain} = 10,040 \times 10^{-0.022H} \text{ psi}$$

where H is the moisture content in per cent. Accordingly, a piece of Sitka spruce containing a normal moisture content has only half the crushing strength of a bone-dry sample.

Since the specific gravity of a specimen of dry wood is a measure of the amount of wood substance it contains per unit volume, it is also an index to strength properties. In general, the greater the gravity, the greater the strength. Some properties, such as maximum crushing strength, are almost linear functions of the gravity. Others increase more rapidly. For example, modulus of rupture varies roughly as the 1.25 power and hardness as the 2.25 power of the gravity. Average relations of specific gravity to strength in the green and air-dried conditions are shown in Table 9-15.

The following function has been established experimentally:

$$E = K(\rho - b) \quad (9-14)$$

where E is Young's modulus, ρ the apparent specific gravity, K a constant depending on the moisture content, and b a constant characteristic for the species. K decreases as the moisture content increases. b presumably represents that portion of the total volume which is ineffective in resisting elastic deformation.

If wood stock, not too thick, is treated with steam, the plasticizing action is sufficient to permit it to be bent into curved shapes. However, this treatment leaves the wood internally stressed, and the tendency to flatten out to the original shape is very marked.

TABLE 9-15. SPECIFIC-GRAVITY-STRENGTH RELATIONS IN WOODS
 (ρ is the specific gravity, oven-dry, based on volume at moisture condition indicated)

Property	Moisture condition	
	Green	Air-dry (12 % moisture content)
Static bending:		
Fiber stress at proportional limit, psi.....	10,200 $\rho^{1.25}$	16,700 $\rho^{1.25}$
Modulus of rupture, psi.....	17,600 $\rho^{1.25}$	25,700 $\rho^{1.25}$
Work to maximum load, in.-lb/cu in.....	35.6 $\rho^{1.75}$	32.4 $\rho^{1.75}$
Total work, in.-lb/cu in.....	103 ρ^2	72.7 ρ^2
Modulus of elasticity, psi.....	2,360,000 ρ	2,800,000 ρ
Impact bending:		
Fiber stress at proportional limit, psi.....	23,700 $\rho^{1.25}$	31,200 $\rho^{1.25}$
Modulus of elasticity, psi.....	2,940,000 ρ	3,380,000 ρ
Height of drop, in.....	114 $\rho^{1.75}$	94.6 $\rho^{1.75}$
Compression parallel to grain:		
Fiber stress at proportional limit, psi.....	5,250 ρ	8,750 ρ
Maximum crushing strength, psi.....	6,730 ρ	12,200 ρ
Modulus of elasticity, psi.....	2,910,000 ρ	3,380,000 ρ
Compression perpendicular to grain:		
Fiber stress at proportional limit, psi.....	3,000 $\rho^{2.25}$	4,630 $\rho^{2.25}$
Hardness, lb:		
End.....	3,740 $\rho^{2.25}$	4,800 $\rho^{2.25}$
Radial.....	3,380 $\rho^{2.25}$	3,720 $\rho^{2.25}$
Tangential.....	3,460 $\rho^{2.25}$	3,820 $\rho^{2.25}$

MARKWARDT, L. J., *Proc. Am. Soc. Testing Materials*, **43**, 435 (1943).

940. Native Wood as a Structural Material. Native wood is particularly interesting in that more than any other structural material it exhibits exceptional merit in some respects and glaring weakness in others. The case may be summarized as follows:

The advantages of wood are that

1. It possesses excellent moduli and elastic properties, which permit it to be stressed almost to the point of break without permanent set.
2. It has excellent modulus-weight ratios (Table 9-9).
3. It is a naturally expanded material so that strengths, moduli, gravities, and figures of merit can be selected or varied to suit different structural needs.
4. It possesses excellent energy and vibration damping characteristics.
5. It is a thermal and electrical insulator.
6. It does not corrode as do metals.

The disadvantages of wood are that

1. It lacks strength balance owing to its anisotropy.
2. It lacks strength in compression and shear.
3. It is nonuniform in quality owing to growth factors and is undependable because of gross flaws such as knots and pitch pockets.
4. It lacks resistance to moisture, which results in serious fluctuations in strength, elasticity, and dimensions, checking, cracking, warping, swelling and shrinking, loosening at joints, decay, and attack by termites.

METHODS FOR IMPROVING WOOD

Various techniques have been developed for eliminating or minimizing the shortcomings of wood while preserving its desirable features. Some of these techniques involve combination of the wood with synthetic resins. The resulting products are among the most important developed through high-polymer technology.

941. Cutting into Veneers or Plies. By cutting native wood into thin sheets or veneers and then assembling such layers with adhesives, various wood products may be made. *Plywood* consists of alternate layers of wood veneer and glue, with the grains of neighboring veneers crossed, most often at right angle. To prevent excessive warping, plywood always contains an odd number of plies so that the grains of the two outermost plies, called the *faces*, run parallel. The inner layer or layers are called the *core*. In *laminated wood* the veneers or layers are glued together with all the grains running parallel. Plywoods and laminated woods may be *natural-density* or *high-density*, depending on how much heat and pressure are applied during manufacture.

The mere cutting into layers makes it possible to reshuffle the wood substance in such manner that originally localized weaknesses and flaws are distributed, a material of greater strength, uniformity, and dependability being the result. Moreover, the cross-banding of veneers produces greatly improved strength balance (Table 9-10). Furthermore, all sorts of desirable combinations of cores and faces of different character may be made. Finally, the cutting into thin layers also makes possible the rapid and thorough impregnation of wood with modifying resins.

Ordinary plywood is made by gluing together the layers at pressures of 250 psi or less. The temperature may be room temperature or an elevated temperature, depending on the adhesive. In ordinary plywood the glue is present in minor amount and serves merely as a bonding agent, the finished product consisting merely of alternate layers of wood and glue. By contrast, if the wood is treated with so much synthetic resin that the wood substance becomes substantially saturated with it, the result is a *plastic plywood*. Here the resin is essentially a continuous phase so that the final product is more of the nature of a laminated plastic

rather than wood layers glued together. Plastic plywood is a product strikingly different from and, for many purposes, greatly superior to ordinary plywood.

942. Compressing. Wood, being a naturally expanded structure, is compressible. Compression to one-third the volume approximately trebles tensile and compressive strengths, as well as various elastic moduli, and greatly increases the hardness (Table 9-15). For many applications, these may be advantages.

Compression may also decrease the *rate* of swelling and shrinking, which is also an advantage. However, the total *amount* of swelling, or, as it is called, the *equilibrium swelling*, is potentially increased (Fig. 9-27). Furthermore, there is a tendency for compressed wood to lose its compression when it is swelled by moisture. This latter behavior is called *springback*. Springback results in a permanent increase from the original compressed dimension. These last two items are potentially serious disadvantages of densified wood; and unless means are used to reduce hygroscopicity, springback, or both, compressing wood to a high density is of no real value.

Normal densified wood is untreated wood that has been compressed at temperatures that do not cause plastic flow of the lignin. It can be made from solid wood and also from veneers, preferably glued with synthetic resin. It is unsatisfactory for structural purposes because it swells more than normal wood and soon loses much of its compression through springback.

In Secs 917 *ff.* it was shown that the comparative efficiencies of structural materials on an equal-weight basis are expressible through various figures of merit, E/ρ , E/ρ^2 , or E/ρ^3 , depending on the type of member to be constructed. Should wood ever be compressed if it is to be used on a strength-for-weight basis? It is seen from Table 9-15 that the elastic modulus increases linearly with the specific gravity so that the figure of merit E/ρ remains essentially constant with compression. Hence, for making stable members to withstand axial loads, compressing the wood results in no sacrifice of relative weight efficiency and at the same time yields a material that has the advantages of hardness, higher stiffness, and higher strengths per unit of cross-sectional area. On the other hand, densification of the wood results in a rapid decrease in the values of E/ρ^2 and E/ρ^3 . Consequently, wood should not be appreciably compressed if it is to be applied on a strength-for-weight basis to the construction of members for which E/ρ^2 or E/ρ^3 is the figure of merit (Sec. 924).

943. Resin Treatment. As previously discussed, many of the ills to which native wood is a prey stem from the absorption and release of moisture by the cellulose. Wood that has been so treated that its hygroscopicity has been reduced and its dimensional stability increased

is called *stabilized wood*. The rate of swelling and shrinking, the total dimensional changes involved (equilibrium swelling), and springback must all be considered as factors of the dimensional stability.

In ordinary plywood where the wood layers are cross-bonded, the fiber direction of one ply restrains the across-the-fiber dimensional change in the next ply when moisture is absorbed so that the over-all dimensional change is less than in native wood. However, this mechanical restraint does not actually prevent swelling and shrinking; it merely changes their direction. Thus, ordinary plywood is restrained from swelling to a normal extent in the layer planes but swells in thickness and inwardly into the fiber canals. Indeed, during alternate swelling and shrinking the mechanical restraints imposed by cross bonding lead to internal stresses so great and uneven that ordinary plywood undergoes more warping and face checking than solid native wood. Cross bonding is therefore only a superficially stabilizing factor.

Wood may be treated with a solution of polar polyfunctional monomers capable of penetrating into the cell-wall structure of the wood and subsequently condensing *in situ* so that the wood becomes loaded with water-insoluble space polymers. For this purpose, phenol-alcohol resinoids (Sec. 1613), which condense to phenol-aldehyde space polymers, and methylol and dimethylol ureas (Sec. 1437), which condense to a urea-resin space polymer, have been widely employed. Evidence indicates that cross-linkage occurs not only among the resinoid monomers but also between them and the cellulose and lignin of the wood. These changes in the chemical nature of the wood, together with the restraints imposed by the intimate primary-valence cross-linking throughout the structure, result in comparatively nonhygroscopic stabilized wood. Uncompressed wood that has been stabilized in this fashion is called *impreg*. Since thick sections are difficult to impregnate completely, the process is usually applied to veneers or relatively thin solid wood members. The most effective stabilizing resins at the current writing are the phenol-aldehydes. After impregnation, the wood is dried and heated to 200 to 250 F to cause polymerization to a C-stage resin. This reduces equilibrium swelling to about 30 per cent of normal. (Urea-aldehyde resins are less water-resistant than the phenolics and reduce the swelling only to 60 per cent of normal.) Phenolic-resin impreg has the following advantages over normal wood: greatly improved dimensional stability; reduced swelling, warping, checking, etc.; greatly improved resistance to decay and termites; greatly improved electrical resistance; improved acid resistance; improved compressive and shear strength; greater hardness. The only property adversely affected is toughness, reflected in lower impact strength, the more so as the resin content is increased.

The phenol alcohols and dimethylol urea solutions used in making

impreg exert a very strong plasticizing action; so much so that flat stock or even two-by-fours of the solution-soaked wood can be bent and twisted readily into intricate shapes without setting up any appreciable internal stresses. Consequently, after polymerization of the resin has occurred, there is very little tendency for these pieces to spring out of shape, a great advantage over curved structural members made by steaming and bending untreated wood products.

In some instances, notably with the urea resinoids, impregnated veneers can be dried and heated till the resin has polymerized to a B-stage. Thereafter, the veneers can be laid up and, by the application of heat and pressure, can be used without any additional adhesive to form plywood. In other words, the stabilizing resin serves also as adhesive, making the treated veneers self-bonding.

Wood can also be impregnated with linear polymers, but the resultant products are generally not so useful. Without primary-valence restraints due to cross-linkage, the wood is not stabilized to the same degree. Furthermore, linear polymers do not possess the high compressive strengths and creep resistance of space polymers. Consequently, they do not improve the normally low compressive strength of the wood as do the phenolic resins, a matter of vital importance in many structural applications; nor do they impart the same degree of hardness to the product.

Compreg is wood that, like *impreg*, has been treated with a dispersion of resin-forming molecules and then, while in the plasticized condition, has been subjected to simultaneous heat and pressure until the resin mutates. It resembles *impreg* in that there has been an interaction between the wood and resin molecules and the formation of space polymer within the cell-wall structure. It differs from *impreg* in that it is a compressed product of higher than natural density, the final density depending on the pressure employed.

The older *compregs* were first made in Europe by treating wood with alcoholic solutions of low-polymeric phenolic resins. The later *compregs*, originally developed at the U.S. Forest Products Laboratory, are made with aqueous solutions of the same polyfunctional phenolic resinoids employed for *impreg*. The alcohol-soluble phenolic resin of the older form is prepolymerized to the stage where it does not penetrate the cell walls and bond intimately to the polar groups of the wood, and as a result the wood is stabilized to a relatively minor extent and exhibits considerable springback. Furthermore, the solution does not plasticize the wood very highly, so that pressures of 2,500 psi or greater are required to compress the product to the virtually ultimate density (*e.g.*, a specific gravity of 1.3 to 1.4). By contrast, the water solutions of resinoids used for the Forest Products Laboratory *compregs* penetrate completely so

that resin formation and bonding to the cellulose takes place all the way through. The latter form of compreg is therefore much more stable, and it is possible to make it with negligible springback. Furthermore, the plasticizing action of the solution is so great that compression to a gravity of 1.3 to 1.4 is attainable with pressures of 1,000 psi or less; indeed, many woods may be compressed to half their original volume under pressures as low as 250 psi. This makes possible the compression of compreg faces and their simultaneous assembly with a core with but slight compression of the core. The resulting sandwich has the advantage of low over-all weight, expanded center, excellent figures of merit, and hard, moisture-resistant, stable faces.

An important feature of the compreg treatment is that it can be applied to a great variety of woods in laminated, plywood, and even solid form. Thus excellent products can be achieved with normally inferior species such as cottonwood.

The strength, moduli, figures of merit, and density of compreg may be varied depending on the degree of compression and the amount of resin added, in accordance with the general principles enumerated in Sec. 935. Both resin content and molding pressure pass through optimum values after the manner shown in Table 9-13 for a resin-impregnated compressed high-strength paper laminate called *papreg*. Impreg may, of course, be considered as a limiting case, *i.e.*, a "compreg" that has been subjected to zero compression.

Parallel-laminated and cross-banded phenolic-resin compregs are among the very strongest organic-polymer materials of construction developed at the current writing. Tensile strengths of 40,000 psi and elastic moduli of 5×10^6 psi are readily attainable in the parallel-laminated products. They have opened up a new range of structural applications for wood products, for these exceptional strengths are combined with dimensional stability, low specific gravity, and low creep rates (Table 9-12). Because of its springback, the older type of compreg is called *unstabilized*, while that developed at the Forest Products Laboratory is known as *stabilized compreg*.

Stable compreg exhibits all the general improvements shown by impreg (see above). Furthermore, water absorption and swelling are small and at the same time very slow, *e.g.*, 4 to 7 per cent increase in thickness on highly prolonged immersion in water at room temperature. Springback is negligible. As with impreg, one mechanical property, the impact strength, is adversely affected. (Unstabilized compreg has a somewhat higher impact strength.)

In impreg and compreg the stabilizing resin is a continuous phase. When pressed between highly polished platens during manufacture,

compreg has a lustrous varnishlike finish. Indeed, a phenolic-resin compreg is, in a sense, varnished all the way through so that, if the surface finish is scratched or marred, it can be completely restored merely by sanding and buffing. The phenol-aldehyde finish is not damaged by alcohol. What is more, surface hardnesses 65 to 90 per cent that of plate glass are attainable. The implications for furniture and woodwork are obvious.

By definition, plywoods made from impreg and compreg are plastic plywoods, the former low-density, the latter high-density.

944. Stabilization by Heat-treatments. Subsequent to the development of impreg and compreg it was discovered that wood may be partly stabilized by heat-treatment alone.

By heating wood at relatively drastic temperatures, 300 to 550 F, in the absence of air, its hygroscopicity is notably reduced, and dimensional stability and resistance to decay are appreciably increased. The evidence indicates that during this treatment water splits out between hydroxyl groups of the cellulose with the attendant formation of ether cross-links. Uncompressed wood that has been thus stabilized is called *Staywood*. The improvements noted above are gained at the expense of darkening of the wood and losses in strength, most notably, impact strength. However, reductions of 50 per cent in hygroscopicity and swelling may be effected without strength losses serious enough to interfere with some important applications.

If normal wood is held during compression at temperatures high enough to cause flow of the lignin and then cooled before the pressure is released, a product which does not lose its compression on subsequent swelling by moisture is obtained. Such heat-stabilized compressed wood is called *Staypak*. The wood should be compressed to a specific gravity of at least 1.3, typical conditions being 2,000 psi and 300 to 360 F. Although its equilibrium swelling is *more* than that of normal wood, it exhibits very little springback, returning to its original compressed thickness on drying to the original moisture content. This is attributed to the fact that the flow of the thermoplastic lignin relieves internal stresses set up during the pressing process. Although the equilibrium swelling of Staypak is very great, exceeding that of normal wood, this is not so serious as one might think since the *rate* of swelling is very low. It swells so slowly that dimensional changes and warping are negligible for most applications. It is debarred only from underwater or prolonged high-humidity uses. Staypak can be made from both solid wood and veneer assemblies.

Staypak shows little resistance to termites, and its shear strength parallel to the grain is appreciably lower than that of compreg of com-

parable gravity. But where these features are not important, its structural potentialities are very great, for its impact strength is roughly double and its tensile and bending strengths about 25 per cent greater than those of compreg of comparable density.

945. Acetylation. When wood is treated for several hours at 200 F with the mixed vapors from a 20 per cent solution of pyridine in acetic anhydride, it undergoes a nonpermutoid type of acetylation. The pyridine acts as both swelling agent and catalyst. Hydroxyl groups of both the cellulose and lignin are converted to less hygroscopic acetate groups. If the process is carried to about a 20 per cent acetyl content, it is found that the acetylated wood has been considerably stabilized, the swelling in water being only about 30 per cent of that of untreated wood. Water-vapor absorption at 80 F and 80 per cent relative humidity is only about four-tenths that of untreated wood. Resistance to decay and shipworms is improved. The volume of the acetylated wood is permanently greater than that of the native wood owing to the bulking action of the acetyl groups. These improvements are attained without significant losses in strength. The treatment is best applied to veneers of $\frac{1}{8}$ in. thickness or less.

DYNAMIC PROPERTIES

946. There is in man a compelling demand for ever higher speeds. Speed brings with it vibration, resonance, and impact and increases the importance of dynamic properties in the design of structural parts. In many cases it is not possible even qualitatively to evaluate a design or make a significant comparison of structural materials on the basis of static strengths alone. As is well known, if a cyclic stress excites resonance vibrations, as often happens in high-speed equipment, the actual dynamic stress set up may be many times greater than the exciting stress and is a common cause of failure. A survey made in 1930 showed that over 95 per cent of automobile structural failures were caused by dynamic forces.

947. Main Types of Dynamic Stress. The most common types of dynamic stress (Fig. 9-28) are the following:

1. *Alternating stress*, which fluctuates, usually sinusoidally, between two limits. Vibrations usually induces such stress. An alternating

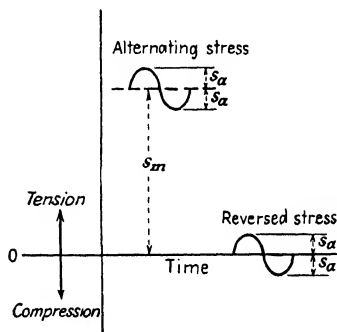


FIG. 9-28. Types of dynamic stress.

stress is characterized by both a mean stress s_m and an alternating component s_a .

2. *Reversed stress*, which reverses in sign during part of the cycle. It usually refers to the special case of alternating stress in which the mean stress is zero, *i.e.*, the stress alternates between two limits equal in magnitude and opposite in sign.

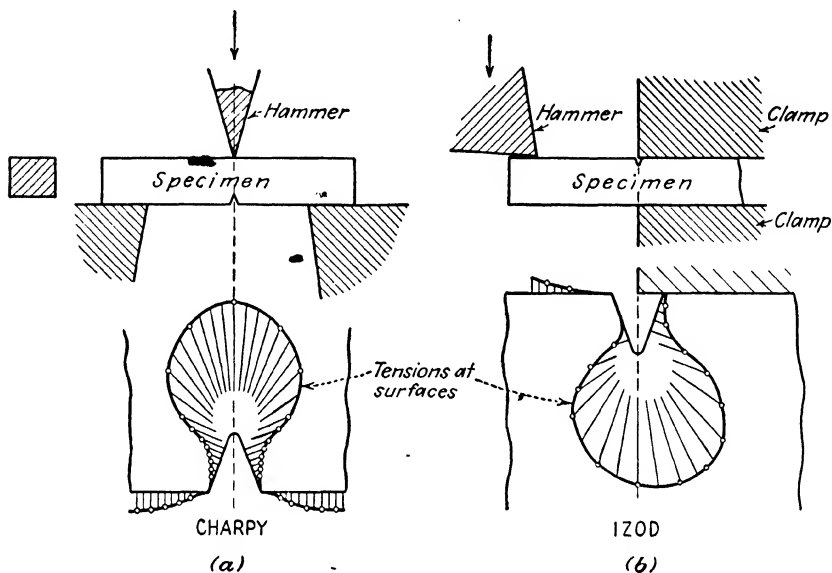


FIG. 9-29. Stress distributions at notch in impact test. (a) Simple beam (Charpy-type test). (b) Cantilever beam (Izod-type test). [D. R. Morey, *Ind. Eng. Chem.*, **37**, 255 (1945).]

3. *Impact stress*, which is characterized by a high rate of change with time and is nonrepetitive. On impact, the kinetic energy of colliding bodies is absorbed by deformations in the material.

948. Impact Resistance. The impact strength of a plastic product is determined in accordance with A.S.T.M. Standard D 256. A specimen is fixed into position either as a cantilever beam (Izod method) or as a simple beam (Charpy method). In either case, a pendulum striker is released from a position such that the linear velocity of the striking edge at the moment of impact with the sample is approximately 11 ft per sec. Means are provided for determining the impact value, which is the energy expended by the machine in breaking the specimen. This value is the difference between the energy in the pendulum blow and the energy remaining in the pendulum after breaking the specimen. Determinations should be made on both notched and unnotched samples. Notch sensitivity is particularly high for impact.

The Izod and Charpy methods yield different results; among other things, the stress concentration on the specimen is different (Fig. 9-29).

949. Brittle Fracture. It will be recalled that the flow or creep-curve equation of a solid contains three main terms and that, upon the application of a given external stress, the total deformation at the end of time t is the sum of an instantaneous elastic, a retarded elastic, and a viscous (permanent) deformation (e.g., Fig. 7-31, page 303). The time t is often called the *action time*.

In equations representing the stress-strain-time behavior of a solid, e.g., Eqs. (7-24) and (7-26), the terms expressing retarded deformations involve the ratio t/λ , which is the ratio of the action time to the relaxation time for a particular type of structural element or particle in the solid. It follows from inspection of an equation such as (7-26) that if the action time is extremely short, as in impact, flow is reduced or eliminated. The solid tends to behave as a Hookian body, elongation at break is relatively small, and the energy absorbed in the process of rupture (area under stress-strain curve) tends to be small. In other words, application of load under impact conditions tends to result in brittle behavior. Indeed, impact leads to a characteristic brittle fracture in a material that otherwise undergoes plastic flow or a long neckdown at low rates of loading. This is aptly illustrated by pitch, which shatters under a hammer blow but flows extensively if load is applied slowly.

It is also well known that brittle behavior is fostered by decrease in temperature, a phenomenon that may be explained in the following terms: Flow processes such as occur in solids require activation and are expressed by an Arrhenius type of function (Sec. 727). The relaxation time in a stressed solid is thus strongly temperature dependent and is proportional to $e^{U/RT}$. Hence, low temperature results in long relaxation times; the ratio t/λ is reduced, and flow once again tends to be eliminated and brittle behavior accentuated. We have, therefore, a theoretical basis for what is well known experimentally, *viz.*, that increase in velocity and decrease in temperature both act toward lessening flow and causing brittleness.

950. Quantitative Relations. It follows from the above that brittle fracture will result when load is applied so fast that flow cannot occur. Let l be the average distance traversed by two structural units that separate from one another, move, and bond again to a next-neighbor unit. This is, of course, flow. The average time required for the process is also the time required for the bond to attain the activation energy U when a given stress is being applied and is approximately proportional to $e^{U/RT}$. The "limiting cohesive flow velocity" is then $Cl e^{-U/RT}$, and this should be a measure of the velocity a hammer or falling weight must have in order to produce a brittle fracture. This theoretical approach has

been substantiated by experiment. For example, in a careful study of the conditions necessary to produce brittleness in soft steel, the following relation was established:

$$V_c = Ke^{-k/T_c} \quad (9-15)$$

where k and K are constants and V_c is the critical velocity and T_c the related critical temperature to produce brittle fracture.

951. Structural Interpretation. Impact strength appears to be a volume rather than a cross-sectional phenomenon, as evidenced by the

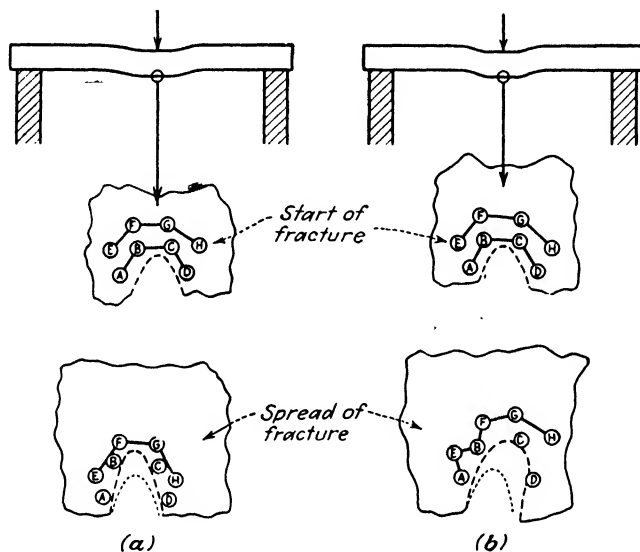


FIG. 9-30. Effect of heterogeneity in bond properties on impact strength. (a) Brittle fracture, strain propagated in small volume with steep localized wave front, uniform relaxation times. (b) High impact resistance, strain dissipated over large volume in all directions, wide distribution of relaxation times. [D. R. Morey, *Ind. Eng. Chem.*, **37**, 255 (1945).]

fact that dividing by the cross section does not yield a constant value for specimens which differ in shape. This implies that the impact strength will depend upon how large a volume of the specimen is able to participate in absorbing the energy of a blow. It may be assumed that there is a large absorption volume when the material is capable of rapid distortion without fracture. A structural interpretation may be made as follows:

Consider a crystalline body in which all the structural elements along a given plane are attracted to one another by bonds identical in magnitude, type, extensibility, and relaxation times. As shown in Fig. 7-15a and discussed in Sec. 711, the energy required to remove each atom or molecule from its potential trough is the same, and any yielding under stress will tend to occur sharply. In Fig. 9-30a, two successive layers

of the structural elements in the crystal are shown schematically as A—B—C—D and E—F—G—H. Assume now that under impact a stress is built up just sufficient to break the bonds in A—B—C—D. The crack then starts forward. Either the bonds will not have time to re-form, or they will do so with new neighbors in a symmetrical fashion so that the stress wave will progress in one direction only and will maintain a sharp front. When it reaches the layer E—F—G—H, the process will be repeated. Thus only a small volume of the material will participate in resisting stress; and if this is originally great enough to cause fracture, the fracture tends to continue across the entire specimen. The material is brittle. By contrast, consider an amorphous material or, for example, a linear-polymeric product with crystalline and amorphous regions and perhaps plasticizer. Here the bonding between elements is irregular with respect to magnitude, type, relaxation times, and extensibility. As illustrated schematically in Fig. 9-30*b*, when fracture starts and breaks the bonds of A—B—C—D, A and B have (by assumption) short relaxation times and rebond quickly to next neighbors E and F; but C and D are assumed to possess long relaxation times and to require relatively large amounts of energy to become activated sufficiently to rebond to new neighbors. The right-hand side of the stress front is accordingly pictured to be left open so that the fracture spreads in this direction. As a consequence, the impact fans out, the stress concentration is reduced, and the volume participating in energy absorption is large. The material is tough rather than brittle.

It is thus seen that resistance to impact may be due to strong bonding, the ability to spread impact energy over a large volume, or both. The impact strength of steel is high for the first reason, that of rubber for the second reason. As one would expect, for similar materials impact strength is related to toughness; and, roughly speaking, the greater the area under the static stress-strain curve, the greater also the impact strength. Plasticization decreases bonding energies but also decreases relaxation times and provides a spread of relaxation times. Hence added plasticizer usually increases impact strength and toughness unless carried too far. Figure 9-31 is illustrative. Heat has a similar effect (Fig. 9-32).

The impact strengths of various plastics are listed in Appendix C. In Table 9-16 more detailed data are given on reinforced phenoplasts of the types often used for stressed-member applications. The effect of temperature is shown, and it will be seen that laminated phenoplasts have been made with impact strengths equaling those of light metals.

The impact strengths of soft rubber vulcanizates are enormous compared with those of rigid polymers. The resilient energy (Table 7-3) as determined from a static tensile test is a measure of the ability to absorb

energy without undergoing permanent deformation. Various materials are compared on this basis in Table 9-17. Owing to the reduction of the number of relaxing elements at impact speeds, impact strengths do not

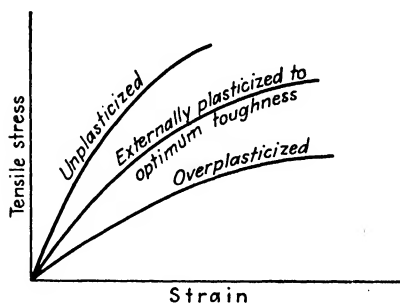


FIG. 9-31. Effect of added plasticizer on toughness and impact strength of a thermoplastic.

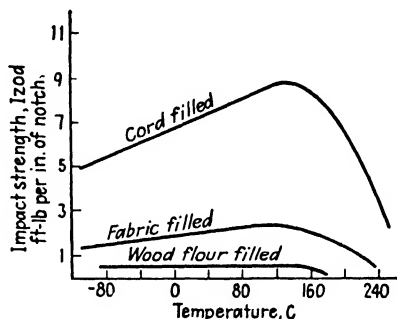


FIG. 9-32. Variation of impact strength of a phenolic with temperature and filler. [C. H. Whillock and R. H. Haslanger, *Modern Plastics*, 19, 70 (June 1942).]

show close quantitative correlation with these statically determined resilient energies.

TABLE 9-17. RESILIENT ENERGIES ON AN EQUAL-WEIGHT BASIS

Material	Resilient Energy, ft-lb/lb
Gray cast iron.....	0.4
Soft steel.....	3.1
Phosphor bronze.....	4.1
Rolled aluminum.....	7.6
Tempered spring steel.....	95
Hickory wood.....	122
Soft vulcanized rubber.....	14,000

As one would expect, impact strength is particularly sensitive to notch effects as well as localized stresses "frozen into" the material during manufacture (Secs. 932 ff.).

952. Impact Fatigue. The impact strength ordinarily quoted is based on a single blow. Such a single-blow impact strength is no more informative about ability to withstand shock than a single static-stress cycle would be in describing behavior under frequently repeated cyclic stress. It is important to know how well a material will withstand repeated impact and to determine what might be called an "impact-fatigue limit," *i.e.*, an impact with which a material can be struck indefinitely without measurable damage. Realization of the need for such data has led to recent exploratory experimentation in this direction. Table 9-18 gives data for repeated-blow impact strength as a percentage of single-blow impact strength. A falling-ball method of measurement was used.

TABLE 9-18.—RELATIONSHIP BETWEEN SINGLE-BLOW AND REPEATED-BLOW IMPACT STRENGTH

Material	Relation of Repeated-blow Impact Strength to Single-blow Im- pact Strength, %
Acrylate resin:	
Compression-molded.....	50
Injection-molded.....	60
Cast.....	41
Polystyrene, compression-molded.....	40
Hard-rubber.....	22
Nylon, injection-molded.....	58
Cellulose acetate-butyrate, injection-molded:	
Hardness S2.....	3.6
Hardness MS.....	5.7
Hardness H, Blend A.....	4.5
Hardness H, Blend B.....	10
Phenolic compound, compression-molded.....	27
Phenolic laminate, paper base.....	50
Phenolic laminate, fabric base.....	45

From an unpublished report, Bell Telephone Laboratories. *

953. Behavior under Cyclic Stress. As indicated in Sec. 710, in an ideally elastic Hookian body the deformation accompanying an applied alternating stress is instantaneous and would always be in phase with the stress. Such a body would have no hysteresis loop, and no energy would be absorbed during a stress cycle. Since the damping capacity of a material is defined as its ability to absorb applied mechanical energy and dissipate it as heat, it follows that the hysteresis loop is a measure of the damping capacity. All real solids exhibit imperfectly elastic behavior, and it may be said in general that, the further a solid departs from perfect elasticity, the larger its hysteresis loop and damping capacity are likely to be.

Consider the mechanical model of Fig. 7-31, page 303. At extremely high frequencies the viscous elements will be effectively "frozen," and the behavior of the system under cyclic stress will be controlled by the elastic elements (springs). The material will behave like an elastic solid, and the deformation will be in phase with the applied stress, the angle of lag being zero. By contrast, at extremely low frequencies, the system will always be completely relaxed owing to creep, exhibiting mechanical behavior akin to that of a viscous liquid devoid of stiffness. Again the deformation will be in phase with the applied stress, the angle of lag being zero. At intermediate frequencies where the relaxation is neither zero nor complete, the deformation will lag behind the applied cyclic stress

and part of the mechanical energy applied during a stress cycle will be absorbed and dissipated as heat. At some particular frequency the angle of lag and energy absorption will reach a maximum. In accordance with this picture, as the frequency of an applied cyclic stress increases from zero to infinity, the apparent stiffness of the material should increase continuously while the angle of lag and hence the damping capacity should rise to a maximum and then decrease again. It also follows that damping capacity and creep should be interrelated, poor creep resistance being in general accompanied by high damping capacity.

The above correlations between frequency, damping, and apparent stiffness (elasticity) assume temperature constancy. In practice, owing to the very absorption of energy during cyclic stressing, the temperature of the material rises above that of the surroundings. The extent of this rise will depend upon the size of the hysteresis loop, the number of cycles per unit time (frequency), the thermal conductivity of the material, the ambient temperature, and the rate of heat transfer from the stressed sample to the surroundings. Since temperature rise results in both lower apparent stiffness and greater elongation for a given reversed stress, it is obvious that certain of these effects may be working against one another and that the actual damping capacity, modulus, and other dynamic properties obtained by test are more or less empirical and highly dependent on testing procedure and conditions. So great are the effects of these many variables that unless the conditions of test are reasonably close to actual service conditions they are of little use in making a significant comparison or evaluation from an engineering standpoint.

The frequency at which maximum damping loss occurs, f_{\max} , decreases sharply with rise in temperature, indicating that the relaxation is an activated process (Sec. 727). The activation energy is obtained from the slope of the plot of $\log f_{\max}$ vs. reciprocal temperature (Table 7-10, p. 308).

Figure 9-33 is a stress-strain curve for a typical plastic subjected to completely reversed stress between equal limits of tension and compression. Owing to hysteresis effects (associated with creep, internal friction, etc.), the unloading curve AB of the stress cycle lies to the right of the loading curve OPA . The line OP is the Hooke's law region of the static stress-strain curve. Its slope is Young's modulus. The static secant modulus of the material (Sec. 705) between zero stress and stress s_a is given by the slope of OA . The *dynamic modulus of elasticity* E_d , which is the stiffness index needed for calculating behavior under cyclic loading, is different from either of these. It is a mean secant modulus, *i.e.*, the mean stress-to-strain ratio effective during a vibration. Unlike a static modulus, which is a fixed quantity, it varies with the frequency and amplitude of the applied cyclic stress.

The energy absorbed by the material in one stress cycle is given by the area of the hysteresis loop $ABCD$. It is obvious that this area will increase as the amplitude ϵ_a of the cycle increases.

954. The Dynamic Modulus of Elasticity. The dynamic modulus of elasticity E_d must be known in order to calculate damping capacities, resonance frequencies of structures, stability of near-resonant vibrations, deflection constants of vibration springs, etc. It may be determined by

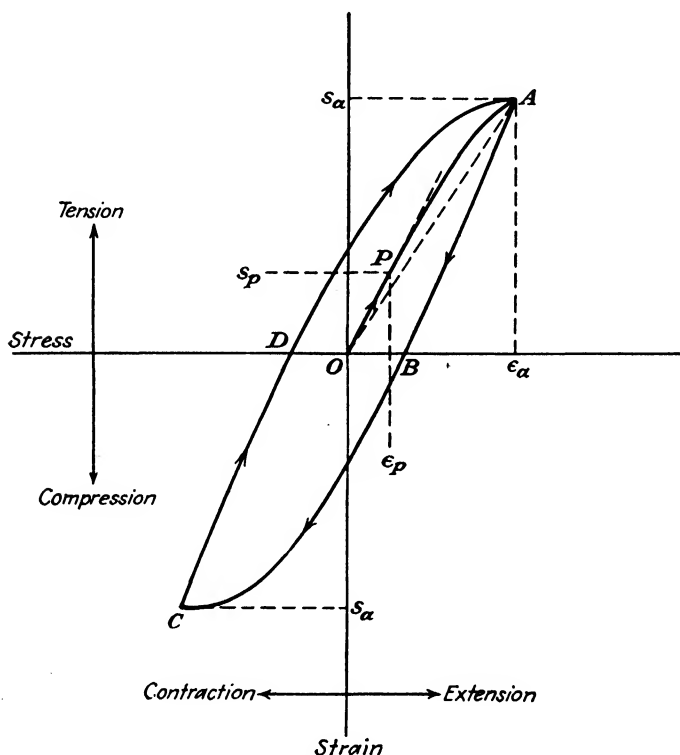


FIG. 9-33. Typical stress-strain relation of a plastic under reversed stress. Slope of OP = static tangent modulus; slope of OA = static secant modulus between stress O and s_a ; OB = extension remaining after part-cycle OAB ; $ABCD$ = hysteresis loop; ϵ_a = amplitude of reversed stress.

measuring the complete hysteresis loop during vibration, the natural frequency of an isolated system under sustained near-resonant vibrations, or the natural frequency of vibration of a freely decaying vibrating system in which the test specimen is the only unknown spring or deflecting member. For the mathematics of vibrational systems and a comparison of various methods of determining dynamic properties the reader is referred particularly to the excellent articles by Lazan and coworkers. If a repeated-constant-force type of oscillator is used in testing, the

dynamic modulus of elasticity may be calculated from the equation

$$E_d = \frac{s_d l}{\epsilon_a} \quad (9-16)$$

where s_d is the maximum direct stress (in tension or compression) induced in the test specimen by the alternating oscillator stress, l the effective length of the test specimen, and ϵ_a the amplitude of the linear sinusoidal vibration of the oscillator.

The variability of the dynamic modulus is of considerable practical significance. Of the factors that influence it and cause it to be different in magnitude from the static modulus, the following appear to be the most important.

1. *Temperature.* Steels are good heat conductors, their elastic moduli near room conditions are very little changed by temperature, and they exhibit comparatively low damping capacities. For these reasons, a steel member under cyclic stress does not heat up very much, nor is its dynamic modulus greatly influenced by the temperature effect.

By contrast, plastics are poor heat conductors, their elastic moduli are highly temperature dependent near room temperature, and they have comparatively high damping capacities, especially at high amplitudes. A plastic consequently heats up considerably during rapid cyclic loading, equilibrium temperatures 20 to 45 C above ambient temperature being not uncommon during testing. This temperature effect contributes toward a gradual decrease in dynamic modulus and increase in amplitude under repeated constant-stress cycles.

2. *Structural deterioration.* Cyclic stress disturbs the structure of a material. In metals it causes cold working, in rigid plastics "fragmentation" of binder, filler, or glue bond. The effect on the dynamic modulus is usually minor in the case of metals but is often extensive in the plastic products.

3. *Hooke's law deviation.* In reporting the static modulus of elasticity it is customary to quote the tangent modulus at zero stress. Since the dynamic modulus is a mean secant modulus for a given cyclic stress and the cyclic stress-strain diagram is curved, showing deviations from Hooke's law, the dynamic modulus is numerically lower than the static modulus. Furthermore, since the deviations from Hooke's law increase with increasing amplitude, there is a tendency for the dynamic modulus to decrease with increasing amplitude.

4. *Loading rate.* The effect of rate of loading upon the elastic modulus has been discussed previously. Although the moduli of stiff metals are very little influenced by loading rate, those of plastics are noticeably affected and in the case of rubbers the percentage increase with increased

rate of loading is extremely high (Table 7-4, p. 274). In dynamic testing the loading rate may be very great. Assuming an alternating stress of 10,000 psi applied at 1,800 cycles per min, the mean rate of loading is 1,200,000 psi per sec.

In summary, the first three factors discussed above tend to produce low dynamic moduli, while the fourth works in the opposite direction. The combined effect of the four factors is quite small for crystalline solids

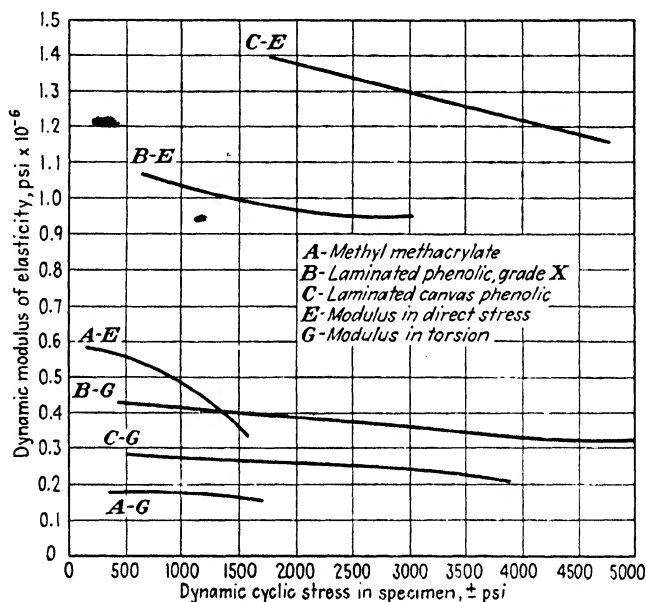


Fig. 9-34. Dynamic moduli of elasticity of plastics under torsional and direct stress. [B. J. Lazan, *Trans. Am. Soc. Mech. Engrs.*, **65**, 87 (1943).]

of high stiffness. In less elastic materials the effect is greater. The dynamic moduli of mild steel and dural vibrating at low stress at about 25,000 cycles per sec are only 2 per cent lower than the static moduli; that of magnesium alloy M is 20 per cent lower at high cyclic stresses. Among plastics the dynamic moduli of laminated phenolics are as much as 30 per cent lower, while that of polymethyl methacrylate is as much as 40 per cent lower than the static modulus. Among rubbers the effect of the fourth factor may predominate, and dynamic moduli may be as much as 40 per cent *higher* than static moduli. In Fig. 9-34 the variation of dynamic modulus with magnitude of cyclic stress as measured by the sustained near-resonance vibration method is shown for a limited number of plastics. Extrapolation to zero gives values within a few per cent of the static moduli. It should be borne in mind that, over the range of

stresses shown in Fig. 9-34, the curves for metals such as steel and dural are practically straight horizontal lines.

955. Damping Capacity. The damping characteristics of a material may be expressed in various terms obtainable by different methods of measurement. The *damping capacity* D is proportional to the area within the hysteresis loop and represents the energy per stress cycle dissipated as heat. It usually is expressed in inch-pounds per cycle.

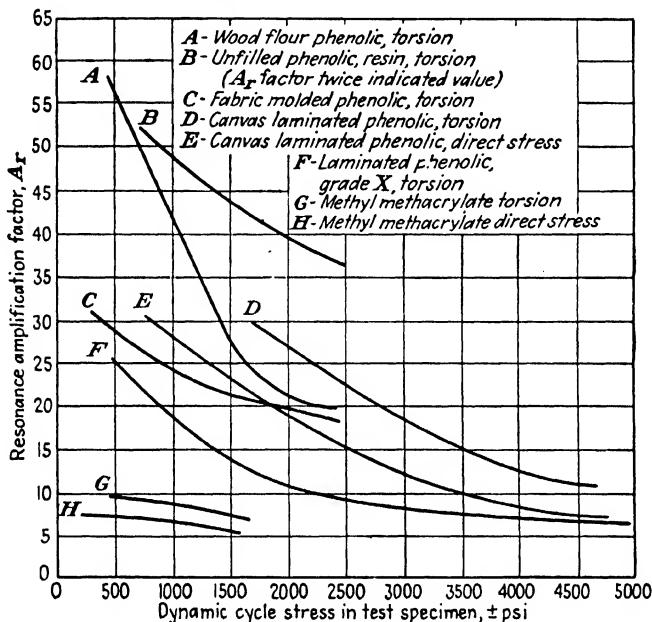


FIG. 9-35. Resonance amplification factors of plastics under torsional and direct stress. (B. J. Lazan and A. Yorgiadis, in "Symposium on Plastics," Am. Soc. Testing Materials, 1944.)

The *specific damping capacity* ψ is the ratio of the energy loss D to the potential, or strain, energy possessed by the specimen when deformed to the position of maximum dynamic stress s_a of the cycle. In terms of Fig. 7-13, page 274, it is the ratio $D/(D + R)$ and may be obtained from the following equation:

$$\psi = \frac{2E_d D}{s_a^2} \quad (9-17)$$

The *logarithmic decrement* δ is the natural logarithm of the ratio of the amplitudes of two successive vibrations of an isolated system in which the vibrations are allowed to decay freely.

The *resonance amplification factor* A_r of a structure is the ratio of the dynamic stress induced in the part under resonant vibrations to the applied

alternating stress that excites the vibrations. A_r is a reciprocal quantitative function of the damping capacity D . A material with poor damping capacity has a high resonance amplification factor, and vice versa.

The four measures of damping are related as follows:

$$A_r = \frac{2\pi}{\psi} = \frac{\pi s_a^2}{E_d D} = \frac{\pi}{\delta + \delta^2 + \frac{2}{3}\delta^3} \quad (9-18)$$

For many materials, the resonance amplification factor is the most readily determined and most highly reproducible measure of damping.

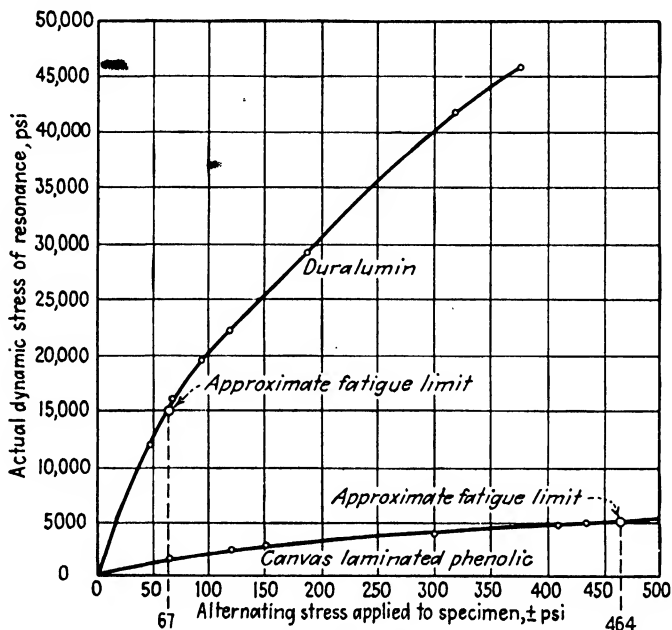


FIG. 9-36. Resonance stress of a metal and a laminated plastic under identical exciting forces. [B. J. Lazan, *Trans. Am. Soc. Mech. Engrs.*, **65**, 87 (1943).]

Values for plastics are shown in Fig. 9-35. For very stiff materials and structures, A_r may be as high as 500 or more, while for rubbers it may be below 10. Generally speaking, the resonance amplification factors of plastics are about one-tenth those of metals and their damping capacities consequently about ten times as high. Figure 9-36 is illustrative. It will be seen that an exciting stress of 200 psi induces a resonance stress of about 3,500 in the canvas-laminated phenolic as against 30,000 psi in the dural.

956. Fatigue or Endurance. If a structural member or test specimen is subjected to a high enough alternating stress through a sufficient number of cycles, it will finally crack and fail. The *endurance* of a material

is its ability to resist this type of failure. It is interesting that the applied cyclic stress which causes failure may be well within the yield strength of the material.

Endurance or fatigue data are usually presented by a so called *S-N* curve. This is a plot of the applied alternating stress against the number of cycles required to cause failure at that stress. The plot is usually semilogarithmic for convenience. For many materials the *S-N* curve is like that shown in Fig. 9-37. There is a *fatigue range* *ABP* in which, the lower the value of the repeated stress, the greater the number of cycles required to produce failure. Finally a point *P* is reached beyond which any further reduction in the stress does not appear to cause failure

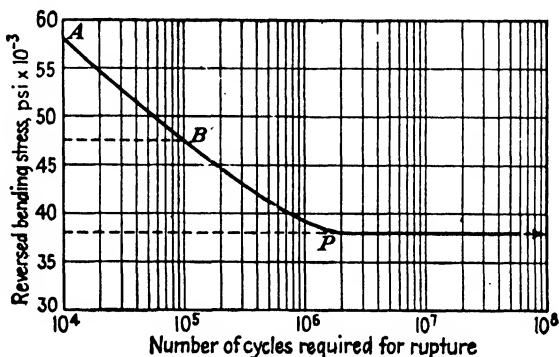


FIG. 9-37. Typical *S-N* curve. SAE 1030 steel.

even if the cycle is repeated indefinitely. (An arrow near the terminus of an *S-N* curve indicates that a specimen has not ruptured during test.) Point *P* is often called the *S-N* transition point, and the stress corresponding to this point is known both as the *fatigue limit* and as the *endurance limit*. Also reported are *fatigue strengths* corresponding to numbers of stress cycles. Thus, for the steel of Fig. 9-37 the fatigue strength for 10,000 cycles to rupture is 58,000 psi; for 100,000 cycles to rupture it is 47,500 psi; its endurance limit is 38,000 psi.

The situation is complicated by the fact that some materials do not possess a definite fatigue limit, no transition point appearing even up to half a billion cycles. In other cases, the *S-N* curve has been found to dip after reaching a temporary plateau. For such materials there is no endurance limit, and only fatigue strengths may be reported.

While fatigue strengths and fatigue limits are helpful semiquantitative guides for design purposes, quoted values must not be taken too literally since many factors influence them. For example, the size, shape, and surface condition of the test specimen exert notable effects (Fig. 9-38). Since specimens will heat up during test in accordance with their damping

properties, it follows that thick specimens will run hotter than thin ones. The surface condition of the specimen will not only influence heat transfer but also determine notch effects (Secs. 931 *ff.*). Indeed, any factor that influences damping as previously discussed will also affect the fatigue value. Fatigue values likewise vary with the type of stress. In a method that applies direct axial cyclic stress all parts of the specimen are subjected to the same maximum stress. On the other hand, in a *bending* fatigue

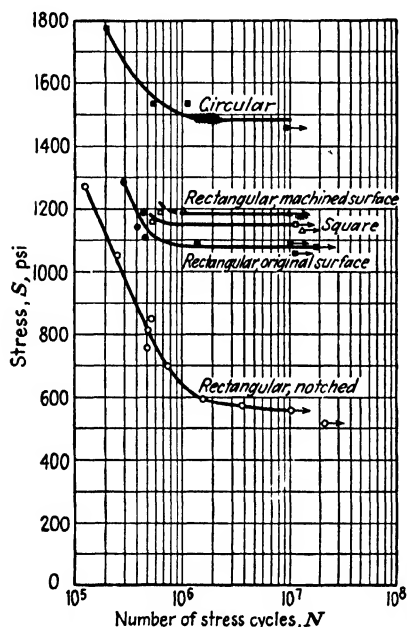


FIG. 9-38. Effects of various factors on the S - N curve of a plastic; cellulose acetate, 26 per cent plasticizer. [W. N. Findley, *Proc. Am. Soc. Testing Materials*, **41**, 1231 (1941).]

test only the surface layers where heat dissipation is good attain maximum stress, while molecules along the neutral axis are scarcely stressed at all. The ambient temperature and the frequency and amplitude employed will also influence the result. Finally, since the ultimate failure is a crack, fatigue strengths, like impact and tensile strengths, are notch-sensitive, the sensitivity in general varying inversely as the toughness and directly as the stiffness. For a discussion of the several methods of fatigue testing the reader is again referred to the papers of Lazan and coworkers.

Table 9-19 contains bending fatigue data on some plastics and metals. The values for structural metals are in general considerably higher than those of plastics, but it should be noted that certain laminated-plastic products exhibit endurance values approaching

those of light metal alloys on an equal-volume basis. A strength-weight comparison is favorable to the plastics.

A high degree of correlation between laboratory fatigue testing and performance in actual service cannot be expected unless the conditions of test, *i.e.*, temperature, size and shape of member, frequency and amplitude of applied stress, etc., are very close to those of actual service, which is not usually the case. This matter is pursued further in Secs. 1321 *ff.*

957. Significance of Dynamic Properties. Hysteresis damping may be either an advantage or a disadvantage. Materials of high damping capacity dissipate a good deal of vibrational or impact energy as heat,

thus eliminating noise to a considerable extent. For example, plastic gears are far less noisy than steel gears.

TABLE 9-19. BENDING FATIGUE DATA
(Unnotched specimens under reversed stress, rotation-beam machine, tested under room conditions unless otherwise specified)

Material	Specific gravity ρ	Mean static modulus of rupture, psi S_b	Modulus of elasticity, $\text{psi} \times 10^{-3}$ E	Cycles $\times 10^{-3}$	Fatigue strength, psi S_a	Endurance ratio S_a/S_b	Specific fatigue strength, psi S_a/ρ
Cellulose acetate.....	1.30	4,900	0.22	100	1,000	0.20	770
Polymethyl methacrylate:							
At 80 F.....	1.18	11,370	0.38	10	2,000	0.19	1,700
At -31 F.....	1.18	18,300	0.66	10	4,800	0.26	4,050
Phenol-aldehyde, cast.....	1.36	12,050	100	4,200	0.35	3,090
Laminated phenolic, grade L:							
Longitudinal loading.....	1.34	21,400	1.60	100	5,000	0.23	3,700
Transverse loading.....	1.34	18,200	1.11	100	4,000	0.22	3,000
Laminated phenolic, grade XX, longitudinal loading.....	1.34	18,400	1.64	100	5,200	0.28	3,900
Compreg. Phenolic resin film-bonded, $\frac{1}{2}$ -in. birch, 35-ply, crossed veneers.....	1.36	29,900	2.29	10	7,500	0.25	5,500
Compreg. Impregnated with 25% by wt of low-polymer phenolic resin; $\frac{1}{2}$ -in. maple, 20-ply, parallel laminated.....	1.37	33,100	3.02	10	12,600	0.38	9,200
Magnesium alloy 57S, extruded and stretched.....	1.81	44,000*	6.50	500	15,000	0.34	8,300
Aluminum alloy 17S-T.....	2.79	60,000*	10.3	500	15,000	0.25	5,400
Mild steel, 0.18% C, hot-rolled..	7.85	61,500*	30.0	10	28,000	0.46	3,550
Chrome-vanadium steel, 0.99% Cr, 0.19% V, heat-treated.....	7.85	201,000*	30.0	10	94,500	0.47	12,000

Data from several sources, notably

LAZAN, B. J., and A. YORGIADIS, in AMERICAN SOCIETY FOR TESTING MATERIALS, "Symposium on Plastics," Philadelphia, 1944.

DIETZ, A. G. H., and H. GRINSFELDER, *ASTM Bull.*, August, 1944, p. 31.

* Ultimate tensile strength.

In selecting a material for a structural part that may undergo near-resonance vibrations in service, damping characteristics as well as fatigue limits must be considered in evaluation. For example, the fatigue limit of dural is about 15,000 psi, while that of a canvas laminated phenoplast is only about 5,000 psi. However, the resonance amplification factor of the plastic is only 11, while that of the dural is 224. From Fig. 9-36 it follows that the largest exciting cyclic stress that the metal can withstand without failure *at resonance* is only $6\frac{7}{464}$, or 14.4 per cent, of that which the plastic will withstand under the same conditions.

High damping capacity can also be a disadvantage by producing lag

in measuring devices and by inducing "whirling" in rotating shafts, but perhaps the most important effect is the heating up of parts of high damping capacity. This is accompanied by a decrease in static-strength characteristics and may also hasten chemical degradation of the structural material. A rubber tire undergoes cyclic stress when a car is in motion. At high driving speeds the temperature rise may attain dangerous values. It is interesting that, in a rubber tire, high vibration and shock absorption (high damping capacity) are required and at the same time it is desired that the tread be not hot-running, which requires low damping capacity.

Although impact strengths cannot as yet be used to predict performance in service in the same analytical way as tensile, compressive, and fatigue strengths, they are nevertheless very useful for qualitative estimation of ability to stand up under handling and general wear and tear.

FACTORS OF SAFETY

958. A structure functions either until it fails in service or is deliberately retired. Failure in service is regarded as an indication of poor design, and rightly so. Thus, if a bridge falls, the engineer is subjected to severe censure; but if it remains standing, he seldom hears complaints to the effect that it is stronger than it need have been. In the past, engineers have applied robust factors of safety to take care of unforeseen service conditions and to guard against the uncertainties involved in the use of so-called "strength values." For this they have sometimes been chided, but, in the light of previous discussion, there is obviously much to recommend this practice. However, the design of high-speed machines and lighter-than-air craft places an enormous premium on low weight and hence requires that much smaller safety factors be employed if efficient operation is to be attained. These more exacting demands make it absolutely essential that we gain more precise knowledge of rheological theory, especially in connection with dynamic stresses.

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See also Appendix A and references at end of Chap. 7.

PARTICULAR TOPICS

See references accompanying tables and figures of this chapter.

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CHAPTER 10

ELECTRICAL, THERMAL, AND OPTICAL PROPERTIES

ELECTRICAL PROPERTIES

1000. Almost without exception, high-polymer products are electrical insulators. They do not permit the passage of electricity when a moderate d-c voltage is impressed across them. This property coupled with ease of molding and fabrication, wide range of mechanical properties, etc., is responsible for their very many electrical applications.

The significant electrical properties of a material used as insulator or dielectric are many and complex.

1001. Volume Resistance. The prime requirement of an insulating material is high electrical resistance under a variety of conditions. All commercial insulators have imperfections that allow the material to pass current when a voltage is impressed. The imperfections may be conducting paths, impurities, and crystal-lattice irregularities. Examples of conducting paths are veins in natural materials such as slate and pores in ceramics. Ionic or metallic impurities, especially when coupled with moisture, obviously will increase the conductivity of an insulator. Although perfect ionic crystals theoretically should not conduct an electric current, actual crystals do to a minor extent. There are vacant places in the lattices and deviations from the theoretical stoichiometrical ion ratios. These imperfections allow current to pass by electronic or ionic migration.

High-polymer products are less subject to conduction by imperfections than ceramic insulators because the structures are not porous (except for plastics with fibrous fillers), their plastic nature makes them more resistant to mechanical shock, and ionic or metallic impurities are more readily controlled. High-polymer products are superior insulators except at high temperatures and applications requiring high strengths and dimensional stability. (In such cases, as for the spark plugs of engines or high-tension insulators, ceramics are superior.)

The generally excellent volume resistivity of organic high polymers varies considerably with chemical composition and filler (Table 10-1), as well as temperature (Fig. 10-1) and moisture content. As expected, the more polar structures have lower resistivities. By use of sufficient carbon of high structure index (Sec. 1315), it is possible to increase considerably the electrical conductivity of a soft rubber. Such conduction is desirable

for the dissipation of static electricity in flooring in rooms containing volatile solvents, in gasoline-truck tires, etc. It is furthermore possible to obtain resistivities as low as 100 ohm-cm, and such stocks are used as

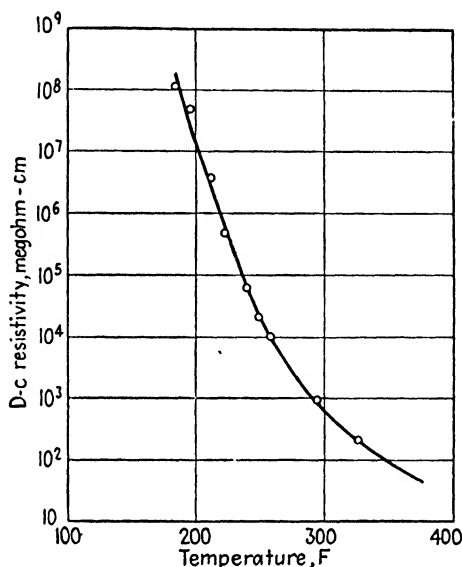


FIG. 10-1. Direct-current resistance as a function of temperature of a molded thermoplast. [T. Hazen, *Trans. Electrochem. Soc.*, **90**, 263 (1946).]

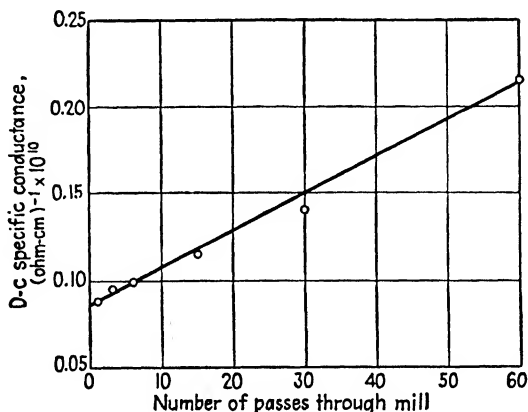


FIG. 10-2. Direct-current conductance of a polyvinyl chloride plastic as a function of milling. [R. M. Fuoss, *Trans. Electrochem. Soc.*, **74**, 91 (1938).]

the electrical conductors in heating pads and aviators' suits. The effect of a processing variable on specific conductance is indicated by Fig. 10-2. It was proved in this case that the increase in conductance was due to hydrogen chloride liberated from the polyvinyl chloride by pyrolysis.

The intercept at zero milling time corresponds to the conductance of an unmilled sample due to original conducting impurities.

Whereas the electrical resistivity of metals increases linearly with increase in temperature, that of insulators decreases exponentially (Fig.

TABLE 10-1. ELECTRICAL INSULATING PROPERTIES OF MATERIALS
(Average properties at room temperature)

Material	Log volume resis- tivity in ohm-cm	Log surface resis- tivity in ohms, at 100 % R.H.	Dielec- tric strength, short time, $\frac{1}{8}$ in. thick, v/mil	Dielectric constant at 1 mega- cycle	Power factor at 1 megacycle
Silica, fused.....	19	8	3,500*	4.7	0.0001
Polystyrene.....	18	10	600	2.5	0.0002
Hydrocarbon wax (paraffin).....	17	10	750*	2.3	0.0004
Styrene rubber.....	16	..	700	2.6	0.001
Polytetrafluoroethylene.....	16	12	500	2.0	0.0002
Mica.....	16	9	1,000*	7	0.0002
Polyethylene.....	15	9	450	2.3	0.0003
Butyl rubber, unfilled vulcanizate.....	15	..	500	2.2	0.004
Hevea rubber, unfilled:					
Soft vulcanizate.....	15	..	450	2.5	0.007
Hard vulcanizate.....	15	..	500	3.0	0.008
Methyl methacrylate.....	15	..	500	3	0.025
Polyvinylidene chloride.....	15	..	400	4	0.04
Buta S, unfilled vulcanizate.....	14	..	500	2.5	0.01
Silicone oils and paste.....	14	..	600*	2.8	0.0004
Silicone rubbers.....	14	13	600*	3-11	0.003-0.04
Polyvinyl formal.....	450	3	0.02
Polyvinyl chloride-acetate, sheet.....	14	9	400	3	0.02
Aniline formaldehyde.....	13	9	600	4	0.007
Nylon, molding.....	13	9	400	4	0.06
Phenol-formaldehyde, mineral filled.....	13	8	450	5	0.007
Phenol-formaldehyde, cast unfilled.....	12	9	400	6	0.04
Neoprene, unfilled vulcanizate.....	12				
Ethyl cellulose.....	12	10	500	4	0.03
Silicone-glass fiber laminate.....	11	..	270	4	0.005
Glass-bonded mica.....	11	7	..	8	0.002
Melamine-formaldehyde.....	11	7	350	7	0.04
Phenol-formaldehyde, paper filled, XX.....	11	9	400	5	0.04
Phenol-formaldehyde, cellulose fabric filled, LE.....	11	8	300	5	0.05
Cellulose acetate, sheet.....	11	9	325	4	0.04
Cellulose acetate-butyrate.....	11	13	325	5	0.03
Vulcanized fibre.....	10	8	200	5-8	0.04-0.08
Urea-formaldehyde, molding.....	9	..	350	7	0.03
Buta N, unfilled vulcanizate.....	8	..	300	11	0.03

Data from various sources, notably

AMERICAN SOCIETY FOR TESTING MATERIALS, "Standards."

PLASTIC MATERIALS MANUFACTURERS' ASSOCIATION, "Technical Data on Plastics," Washington, D.C.

FIELD, R. F., *J. Applied Phys.*, **17**, 318 (1946).

WARNER, A. J., *Elec. Communication*, **22**, 70 (1944).

* 1 mm thick (40 mils).

10-1). This indicates that, in the latter, activation processes are involved (Sec. 229) in the liberation or migration of the conducting particles.

Humidity affects the volume resistance of insulators to markedly different extents. Both the porosity and the polarity of the material are important. Nonpolar materials like polystyrene are unaffected, but polar organic high polymers are sufficiently solvated by the moisture to undergo considerable decrease in volume resistance, the effect increasing roughly with the extent of solvation. Polar inorganic high polymers, such as glass and quartz, are so little solvated that they are substantially unaffected provided that they are nonporous. Porosity invariably permits moisture absorption and lowers the volume resistance. Thus plywood impregnated with a phenol-formaldehyde resin (impreg) has 1,000 times the resistivity at 90 per cent relative humidity than the unimpregnated wood. Some apparently nonporous insulators exhibit a humidity effect owing to a microporous structure, examples being mica and plastics with fibrous fillers. In many cases it is difficult to distinguish between volume and surface effects. This problem is further discussed in Secs. 1002 and 1007.

1002. Surface Resistance. Electricity is carried along the surface of an insulator as well as through the interior. Indeed, the high conductance of a crack is largely due to surface conductance along the walls of the crack. Similarly, the great effect of humidity on porous insulators is largely the result of the surface conductivity of the pores.

The surface conductance of an insulator is negligible for a clean, dry surface but increases very rapidly as any foreign conducting material adheres to the surface. Water, in particular, adheres to the surface of most insulators and is adsorbed under conditions of immersion or high relative humidity. The amount of adsorption is more pronounced with the more polar polymers. This adsorbed water, even though pure initially, easily becomes conductive by contamination with electrolytes such as carbon dioxide from the air, salts in the surrounding moisture, or soluble impurities in the insulation itself.

If no volume absorption takes place, surface conductance changes rapidly with change of humidity. By contrast, volume absorption of water results in a volume conductance and also provides a reservoir which tends to maintain the surface moisture film even though the ambient humidity decreases, so that the surface resistance tends to remain constant.

An important factor is whether a *continuous* film of water forms readily. The formation of such a film is determined by the ease with which water wets the surface, which in turn is measured by the contact angle between the surface and a drop of water on the surface. Only hydrocarbon-type polymers successfully resist the formation of a con-

tinuous film (on a clean surface). For this reason it is customary to coat the surfaces of ceramic-type insulators with a water repellent such as wax or polystyrene. Moisture condenses on such a surface as discrete droplets. Formation of a silicone layer *in situ* has been found particularly valuable for these insulators [Eq. (2-2), page 39]. A similar water-repellent layer is produced by dipping a warm ceramic object into a solution of a nonvolatile liquid silicone, followed by baking to fix the silicone film on the surface.

The surface resistivities of a number of materials at 100 per cent relative humidity are given in Table 10-1. The materials were as clean as they could be in actual use. The high surface resistivity of cellulose acetate-butyrate is probably due to the adsorbed moisture being present as a discontinuous film.

1003. Electrical Breakdown. Electrical insulation fails under high voltages. The *breakdown voltage* of a material is the maximum potential gradient that the material can withstand without breakdown and passage of discharge. The behavior is analogous to that when a solid is mechanically stressed within and beyond its yield point. Thus, the electric intensity at any point in the material is often referred to as the *electric stress*. It is regarded as producing an electric displacement proportional to the stress and the dielectric constant of the material, as long as the stress is less than the critical value; but when this value is exceeded, the electric displacement increases very rapidly and the whole structure of the material becomes unstable and collapses. Furthermore, electrical failure in solids, like mechanical failure, is an accidental phenomenon associated with flaws (or impurities) in the material.

The experimental breakdown voltage, like the yield stress, is not constant but varies with the conditions of test. Thus the electric intensity required to produce breakdown varies with such factors as duration and rate of application of voltage, thickness of test piece, frequency of applied voltage, temperature, size and shape of electrodes, and nature of surrounding medium. Therefore the test conditions must be carefully standardized. The dielectric strength is calculated from the breakdown voltage and the thickness of the specimen at or near the point of rupture and is commonly expressed in volts per mil (0.001 in.) or in volts per millimeter. Breakdown voltage increases with thickness of sample, often reaching a constant value, so that the dielectric strength decreases with thickness (Fig. 10-3).

For quick determinations of dielectric strength a short-time test is used, in which the voltage is increased from zero to breakdown at a uniform, rapid rate (Table 10-1). For somewhat less rapid determinations, laying more emphasis upon the time factor, the step-by-step test is used,

in which the voltage is increased by increments, the voltage being held at each level for a definite time. Nonrigid plastics that exhibit high dielectric and high mechanical strength in thin sections are particularly valuable for insulating tapes. Polytetrafluoroethylene, polyethylene, polyvinyl formal, polyvinyl chloride, and some rubbers can be made into insulating tapes with dielectric strengths of over 1,000 volts per mil in 10-mil thickness.

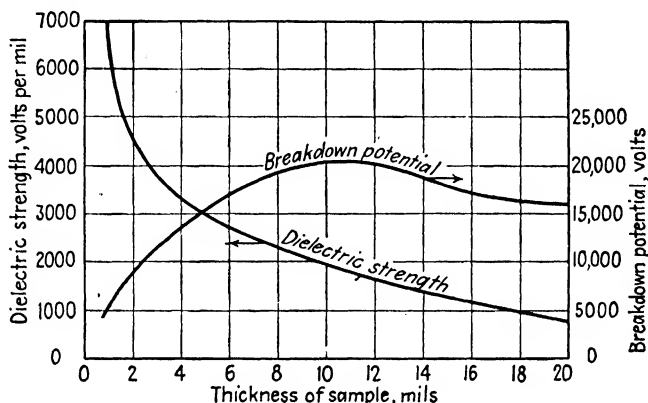


FIG. 10-3. Dielectric strength of styrene rubber. (Dow Chemical Co. pamphlet on Styraloy 22.)

In testing arc resistance, point electrodes are placed on two points of the same surface of the insulator. An arc is then passed between the electrodes. Originally the arc passes through the air; but with time or as the current is increased, the material eventually breaks down and the arc travels on its surface. Polytetrafluoroethylene, ureas, and melamines have particularly good arc resistance.

Even at voltages below the breakdown value, some current passes owing to the volume and surface conductivity. This leakage current is often due to flaws or impurities, which allow paths of current travel. Moreover, during an electrical breakdown (either dielectric-strength test or arc-resistance test) chemical decomposition often occurs, the decomposition products forming a path, or track, which permits subsequent discharges to take place at lower potentials. Polymers of styrene, tetrafluoroethylene and methyl methacrylate, silicones, ureas, and melamines are highly resistant to tracking.

1004. Dielectrics. The qualities of an insulator of importance in a constant-voltage field were considered in the previous section. In an alternating field the phenomena are more complex, particularly when the material is subjected to a range of frequencies. It is necessary to know the electrical properties of a material under the variety of conditions

to which modern devices are subjected in order to determine its suitability for any particular application.

In conductors, under a potential difference a flow of charged particles takes place, and the atoms or molecules of the conductor offer frictional resistance, but elastic effects are absent. An electric conductor has no "electric yield point," much as a Newtonian liquid has no mechanical yield point. In an insulator, on the other hand, if an electric force is applied, there is a restricted yielding or displacement of bound charges, but no flow. The amount of displacement increases with increase of potential. On removal of the external field the charges spring back to their original equilibrium positions. The displacement or charging effect is quantitatively measured by the dielectric constant, so that insulators are also termed *dielectrics*, especially in alternating fields.

The electrical properties of conductors are largely described by the conductance, whereas those of dielectrics are largely described by the dielectric constant. The same molecular structure and ionic processes that determine conductance also control dielectric constant. The conductance of dielectrics is by no means constant and at two different frequencies may not even be of the same order of magnitude. It is therefore sometimes convenient to represent conductance phenomena in dielectrics by other coefficients.

On application of a constant voltage to a dielectric a current flows during the charging process, but this flow decreases with time and shortly becomes zero. By contrast, in an alternating field a current flows through the dielectric by means of periodic displacement of bound charges. This current is termed the *displacement current*. Consequently, alternating currents can be carried by substances that are insulators for direct current. The polarizability of the dielectric, *i.e.*, the relative charge displacement, determines the magnitude of the displacement current. Of course, a d-c conductance will also be present owing to factors discussed in the preceding sections. This ohmic conduction current is superposed on the capacitative current. The ohmic conduction current differs from the capacitative current in its energy effects because it always results in energy dissipation and consequently heat buildup in the resistance. On the other hand, displacement current does not result in energy dissipation in a perfect dielectric since the energy absorbed during passage of the current in one direction is returned on reversal of the current. Mechanical analogy is once again instructive. If a Hookian solid is subjected to cyclic stress, loading and unloading occur along the same path. Theoretically at least, there is no hysteresis loop and no loss of work as heat.

Under a given voltage gradient and frequency, the displacement

current flowing in a material is directly proportional to the dielectric constant. The dielectric constant is conveniently written as the sum of a number of terms corresponding to the types of charges being displaced, as shown in Fig. 10-4. Under very high frequency only electrons are displaced. This *electronic polarization* is obviously present at all

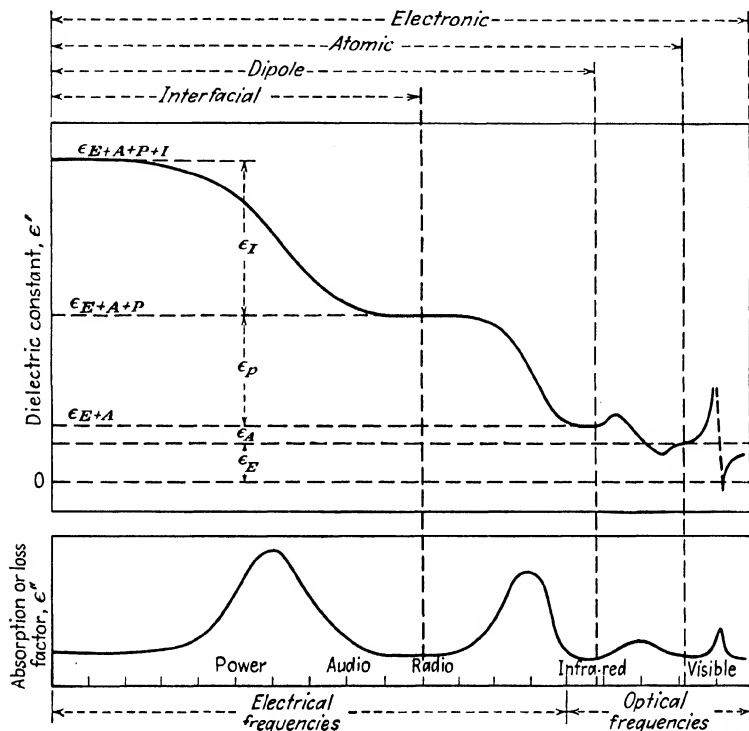


FIG. 10-4. Effect of frequency on dielectric constant and loss factor. [A. J. Warner, *Electrical Communication*, **21**, 180 (1943).]

lower frequencies as well. According to the Maxwell relation, it is measured by the *optical dielectric constant* ϵ_∞

$$\epsilon_\infty = n^2 \quad (10-1)$$

where n is the index of refraction. This equation reveals the interesting and highly important relation between the electrical and optical properties of a material. In some materials, benzene for example, the only polarizable elements are electrons, and the dielectric constant is the same from optical frequencies down to zero frequency. For a nonpolar substance the molar electronic polarization P is given by the Clausius-

Mosotti equation

$$P = \frac{\epsilon_{\infty} - 1}{\epsilon_{\infty} + 2} \times \frac{M}{\rho} = \frac{4}{3} \pi N_0 \alpha \quad (10-2)$$

where ρ is the density, N_0 Avogadro's number, and α the polarizability, and ϵ_{∞} is calculated from Eq. (10-1).

As the frequency is lowered, more massive particles may be displaced. In the near-infrared region, atoms and ions are displaced, giving rise to *atomic polarization* (Fig. 10-4). This is usually small for atoms but may be considerable for ions. When atomic polarization is present, the Clausius-Mosotti equation is expanded to

$$P = P_E + P_A \quad \alpha = \alpha_E + \alpha_A \quad (10-3)$$

In this case the index of refraction must be measured with infrared rays. Both electronic and atomic polarizations occur in dielectrics used for electrical applications because the working frequencies are all below the near-infrared range. The above equations are quantitatively valid for nonpolar substances and for solid polar substances provided that the dipoles do not rotate. As predicted by Eq. (10-2), the dielectric constant of these materials decrease slightly with rise in temperature owing to the decrease in density.

In polar liquids and some polar solids the situation is quite different. They exhibit dielectric constants much larger than the optical value, owing to the presence of dipoles which are free to orient in an applied field (Sec. 210). Thus, the inception of rotation in a polar molecule produces a large increase in dielectric constant (Fig. 5-15, page 178). For the molar polarization of such substances Debye derived the equation

$$P = \frac{\epsilon - 1}{\epsilon + 2} \times \frac{M}{\rho} = \frac{4}{3} \pi N_0 \left(\alpha + \frac{\mu^2}{3kT} \right) \quad (10-4)$$

where μ is the dipole moment, k the Boltzmann constant, T the temperature, and ϵ the dielectric constant. In this case the dielectric constant must be determined in the radio-frequency range (Fig. 10-4) and can no longer be calculated from the optical index of refraction by Eq. (10-1). *Dipole polarization* is also termed *Debye polarization*. It is given by the term $\mu^2/3kT$, which shows it to be highly temperature dependent. Equation (10-4) is quantitatively valid for a gas or a dilute solution of the polar material in a nonpolar solvent and is used for the calculation of dipole moments from dielectric-constant measurements. For polar liquids the polarization calculated from the measured dielectric constant is less than the polarization calculated from the dipole moment, owing to mutual orientation of neighboring dipoles, which hinders their orienta-

tion in the field. A more comprehensive theory for such systems has been elaborated by Onsager and Kirkwood.

In addition to electronic, atomic, and dipole polarizations, a fourth type of polarization, termed *interfacial polarization*, occurs in heterogeneous materials, where the components have different dielectric constants and conductivities. In a composite dielectric the charged carriers, ions or electrons, heap up at the interfaces of the components during each alternation of the electric field and serve to increase the dielectric constant and capacitance. Interfacial polarization is also termed *Maxwell-Wagner polarization*. In most cases interfacial polarization involves larger masses than dipoles, in which case it takes place at lower frequencies (Fig. 10-4). However, if the components are molecularly distributed, *e.g.*, water in cellulose, and especially if one component has a high conductance, the loss due to this polarization may occur at the same frequencies as dipole polarization.

One may summarize as follows: Four kinds of polarization may contribute to the dielectric constant of a material. In increasing order of the average masses of the particles involved, they are electronic, atomic, dipole, and interfacial. The relations are shown in Fig. 10-4. As will be discussed below, the inertia of the particles and the consistency within the material contribute toward determining which are capable of orienting in an alternating field. At the very highest frequencies, only electronic polarizations take place; but in a static field (frequency is zero) all four types of polarization may occur, and the maximum dielectric constant is attained. This will be designated by the symbol ϵ_s . When interfacial and dipole polarizations take place, the dielectric constant decreases markedly with rise in temperature owing to the interference of thermal agitation with conductivity and orientation.

1005. Anomalous Dispersion and Dielectric Absorption. Assume that a dielectric is relatively simple, manifesting only dipole and electronic polarizations. At low frequencies where the direction of the applied field is changing slowly, both the dipoles and the electrons always have sufficient time to orient and remain in phase with the field. Under these conditions, no energy is absorbed by the dielectric (neglecting d-c conductance). Furthermore, the dielectric constant remains constant and essentially equal to the static value, both the electronic and dipole polarizations contributing to it.

If the frequency is now raised to a sufficiently high value, the dipoles, owing to the internal "viscosity" of the material, are completely incapable of following the reversals of the applied field, although electrons still can. In other words, dipole polarization ceases. The dielectric constant under these conditions is constant but now has dropped to the optical

value since it depends only on electronic polarization. Again there is no energy absorption by the dielectric since the electronic polarization is always in phase with the field.

In the range of frequencies between the two postulated above, the dipoles follow the field reversals, but not rapidly enough to remain completely oriented with it. Under these conditions the dipole orientation lags the applied voltage, and in each cycle electrical energy is absorbed, being lost as heat. This range of frequencies is known as the region of *anomalous dispersion*. In it the dielectric constant is not constant but changes with the frequency. It has a value intermediate between the static and optical values. The viscous resistance of the material as expressed by its relaxation time influences the degree to which the dipoles are able to keep in phase with the applied voltage, much as it influences the ability of viscous elements to remain in phase with a cyclic mechanical stress (Sec. 953). At any rate, in the region of anomalous dispersion Debye's equation becomes

$$P = \frac{\epsilon - 1}{\epsilon + 2} \times \frac{M}{\rho} = \frac{4}{3} \pi N_0 \left[\alpha + \frac{\mu^2}{3kT} \left(\frac{1}{1 + j\omega\tau} \right) \right] \quad (10-5)$$

where $\omega/2\pi$ is f (the frequency), τ the relaxation time, and j the 90-deg rotative operator, that is, $\sqrt{-1}$. The lag of dipole orientation behind the field, and hence the energy loss, is greatest when the period of the field is of the same order as the relaxation time. The relation between relaxation time and viscosity is

$$\tau = \frac{K\eta a^3}{T} \quad (10-6)$$

where K is a constant calculable for simple systems such as gases, η the coefficient of viscosity, and a the molecular diameter of a sphere hydrodynamically equivalent to the molecule.

The considerations just adduced apply generally. With each change in the dielectric constant of a material there is a region of anomalous dispersion, and the energy loss becomes a maximum at the point where the rate of change of dielectric constant is greatest (Fig. 10-4); this occurs where

$$2\pi f\tau = 1 \quad (10-7)$$

A dielectric has at least as many relaxation times as regions of changing dielectric constant; and frequently each region has a band of relaxation times. Anomalous dispersion and the region of dielectric loss that always accompanies it are referred to as *dielectric absorption*.

The behavior of a material exhibiting anomalous dispersion can be

represented by placing a conductance in the circuit in parallel with the dielectric. The current may be regarded as composed of two parts, the displacement current across the capacitance, C , which is out of phase with the voltage and does not dissipate any power, and the conductance current through the conductance, G'' , which is in phase with the voltage and which dissipates power. The total current is the vector sum of these two currents.

An additional method of representing the relations in anomalous dispersion is used in discussions on dielectrics. Two quantities are employed. The quantity ϵ' is the ordinary dielectric constant.

$$\epsilon' = \frac{C}{C_0} \quad (10-8)$$

where C is the capacity of a condenser with the dielectric material between the plates and C_0 is the capacity of the condenser in a vacuum (or air). The displacement current is proportional to ϵ' . The quantity ϵ'' is the *loss factor* due to anomalous dispersion and measures the conductance current,

$$\epsilon'' = \frac{G''}{\omega C_0} = \frac{G''}{2\pi f C_0} \quad (10-9)$$

where G'' is the conductance of a resistor that would dissipate the energy lost in the anomalous dispersion, *i.e.*, the conductance current is proportional to ϵ'' . The ratio of conductance current to displacement current is termed the *dissipation factor* and is given by

$$\tan \delta = \frac{\epsilon''}{\epsilon'} \quad \text{or} \quad \tan \delta = \frac{G''}{2\pi f C} \quad (10-10)$$

where the angle δ is termed the *loss angle* and is the phase difference between the total current and the displacement current. The ratio of conductance current to total current is termed the *power factor* and is $\sin \delta$. For small values of ϵ''/ϵ' , the loss angle, the dissipation factor, and the power factor are equal for practical purposes. Table 10-1 lists values of dielectric constant and power factor of various high polymers at high frequencies.

All these considerations apply in a dielectric without a d-c conductance. The latter causes additional loss, and the total conductance is

$$G = G_0 + G'' \quad (10-11)$$

where G_0 is the d-c conductance. The power-dissipation rate in the material is

$$W = E^2 G \quad (10-12)$$

where E is the voltage.

It should be noted further that if a conducting impurity is added to a dielectric an increase in dielectric constant takes place because of the ions which heap up at the interface (interfacial polarization) (Fig. 10-5). Consequently, another region of anomalous dispersion is added, or the loss in an existing region is increased (Fig. 10-6). This means that conducting impurities cause greater losses in a-c circuits than in d-c circuits.

These relations are significant in two major industrial applications, insulators in high-frequency circuits (Sec. 1007) and dielectric heating (Sec. 1008).

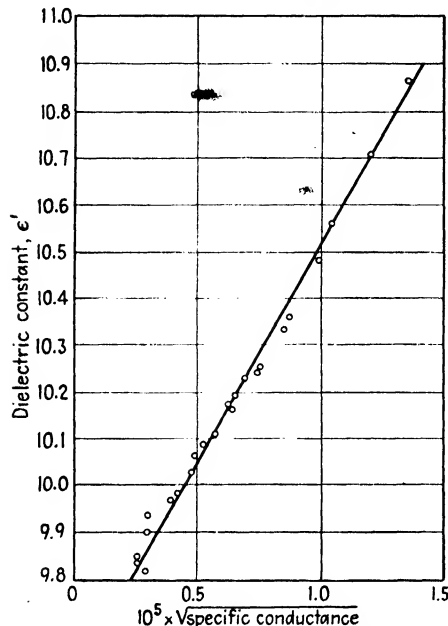


FIG. 10-5. Dependence of 60-cycle dielectric constant of a polyvinyl chloride plastic on d-c conductance. [R. M. Fuoss, *J. Am. Chem. Soc.*, **61**, 2329 (1939).]

viscosity, allowing relaxation to take place more readily, and thus lowering the temperature of the peak in the loss-factor curve at constant frequency (Fig. 3-4, page 83).

The shape of the dielectric-constant curve naturally determines the shape of the loss-factor curve (Fig. 10-8). When the dielectric constant changes rapidly with frequency, the region of absorption is narrow and the loss-factor peak is high. This is the case if all the polarizable complexes of a given type have the same relaxation time. In such a case, for dipole polarization the Debye theory gives

$$\epsilon_M'' = \frac{\epsilon_s' - \epsilon_\infty'}{2} \quad (10-13)$$

where ϵ_M'' is the maximum value of the loss factor, ϵ_s' the highest value of the dielectric constant for the particular region (equals the static value if there are no other regions of absorption), and ϵ_∞' the lowest value of the dielectric constant for the particular region (equals the infinite-frequency value if there are no other regions of absorption). In most dielectrics there is a band of relaxation times distributed about a most prominent value τ_0 according to some law of probability. The effect of a distribution of relaxation times is to broaden the frequency band of dielectric absorption without changing the magnitude of the dispersion and to decrease the magnitude of ϵ_M'' as shown by curves 2 and 3, Fig. 10-8. The broader the distribution, the greater these effects will be.

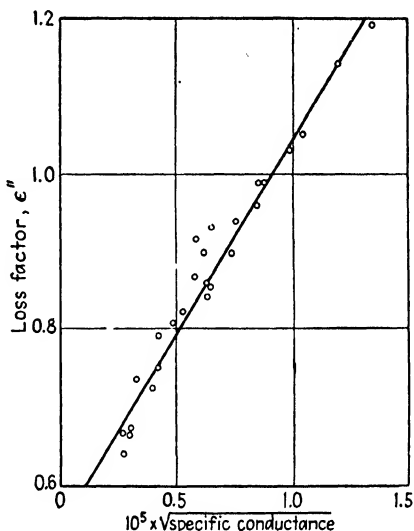


FIG. 10-6. Dependence of 60-cycle loss factor of a polyvinyl chloride plastic on d-c conductance. [R. M. Fuoss, *J. Am. Chem. Soc.*, **61**, 2329 (1939).]

If the dielectric absorption is due to dipole polarization, the value of

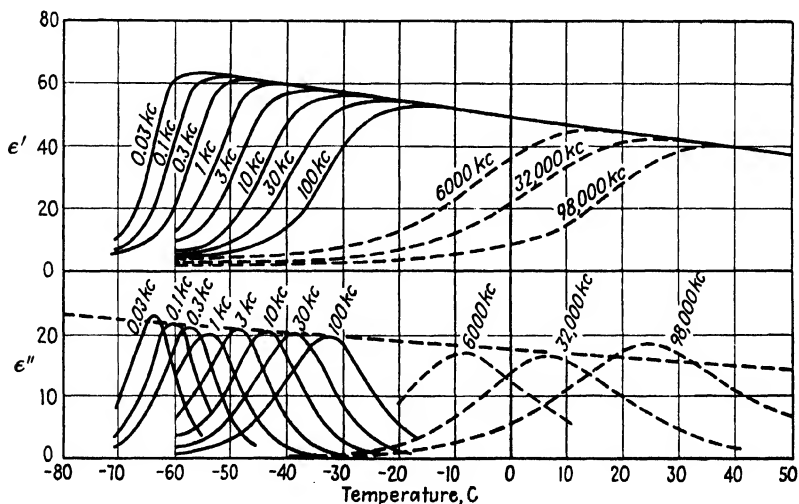


FIG. 10-7. Dielectric properties of glycerol as a function of frequency and temperature. Solid curves are from one set of measurements, dashed curves from another. [S. O. Morgan, *Trans. Electrochem. Soc.*, **65**, 109 (1934).]

ϵ_M'' decreases slightly with rise in temperature (Fig. 10-7). This follows from Eq. (10-13), for ϵ_s' includes dipole polarization and so decreases markedly with temperature, while ϵ_∞' includes only electronic and atomic polarization and so decreases slightly with temperature.

The electrical properties of polyvinyl acetate are given in Fig. 10-9. Evidently the anomalous dispersion is due to dipole polarization. The

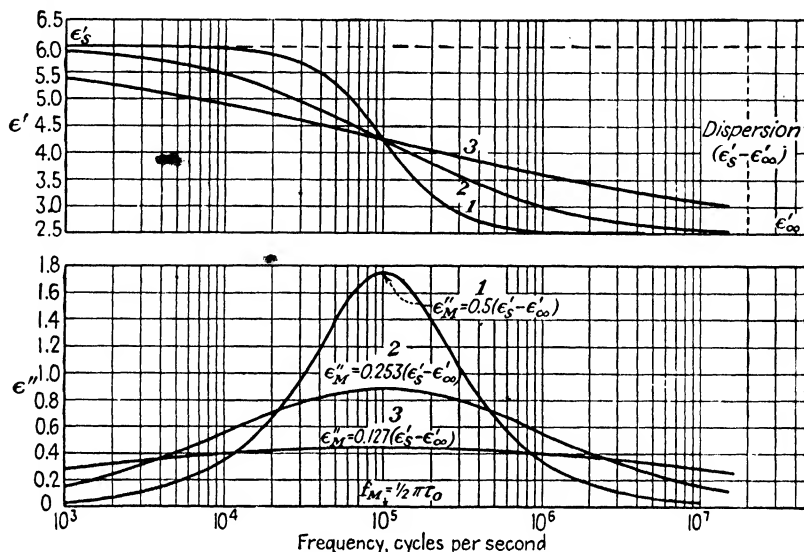


FIG. 10-8. Typical frequency variation of dielectric properties in a region of dielectric absorption. Curve 1: single relaxation time. Curve 2: moderate distribution of relaxation times. Curve 3: broad distribution of relaxation times.

effect of molecular weight is not surprising (Fig. 10-10), the higher molecular weight material having the greater relaxation times. Indeed, this result provides a means of determining relative molecular weights of high polymers, the ratio of relaxation times in this case being the same as the ratio of molecular weights as determined by the solution-viscosity method.

Figure 10-11 shows the electrical properties of halowax, a commercial mixture of chlorinated naphthalenes used as a condenser dielectric. The distinctive feature of these curves is an increase in the value of ϵ_M'' with increasing temperature, which is contrary to the behavior for dipole polarization. The theoretical equations for interfacial polarization show that such a behavior can be accounted for in heterogeneous dielectrics either by a change in the conductance of one component relative to that of the other or by a change in the relative proportions of the components. This indicates that a Maxwell-Wagner polarization is responsible for the dispersion. The fact that the polarization takes place at relatively high frequencies indicates that the components are molecularly dispersed.

Hevea rubber contains few polar groups and the dielectric constant is substantially independent of frequency. However, when rubber is sulfur-vulcanized, the dielectric constant (at constant frequency) increase with increased sulfur content, undoubtedly owing to the highly polarizable sulfur atoms. In addition, as the effect of frequency indicates (Fig. 10-12) a dipole structure is introduced, probably located on the cross-links.

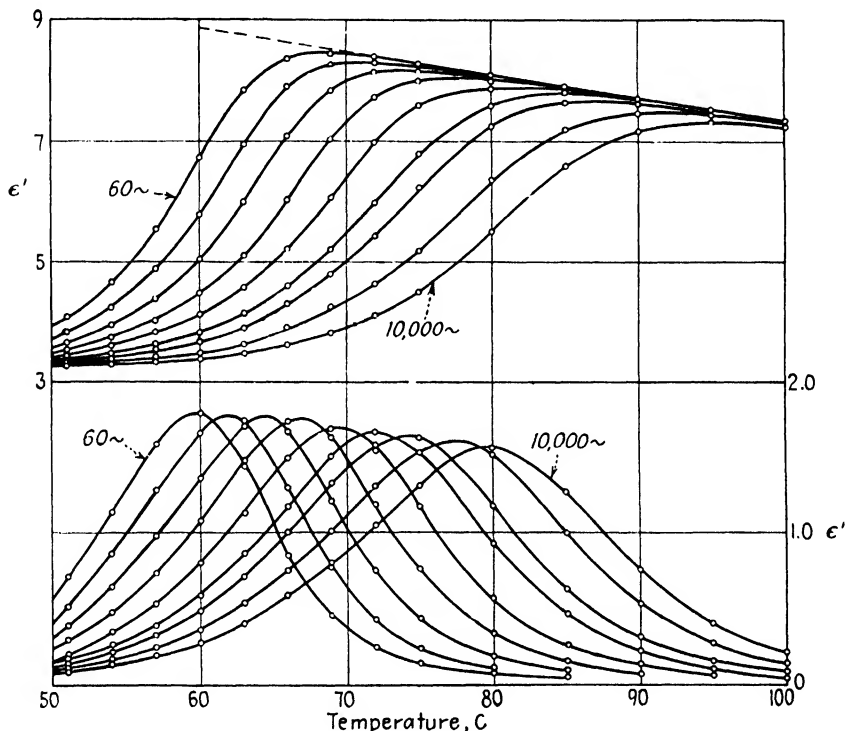


FIG. 10-9. Dielectric properties of polyvinyl acetate as a function of frequency and temperature. [D. J. Mead and R. M. Fuoss, *J. Am. Chem. Soc.*, **63**, 2832 (1941).]

Dielectric relaxation rate (reciprocal of relaxation time) increases exponentially with temperature (Fig. 10-10), indicating that an activation process is involved (Sec. 229). In Fig. 10-13 are plotted logarithmically the relaxation rates at different temperatures against the viscosities at the same temperatures for a number of pure substances. The linear relation between the two is expected, not only from Eq. (10-6) but more generally because viscous flow of liquids also involves an activation process (Sec. 727).

The activation energy of dielectric relaxation in rubber increases with the sulfur content, in harmony with the increased rigidity of the structure.

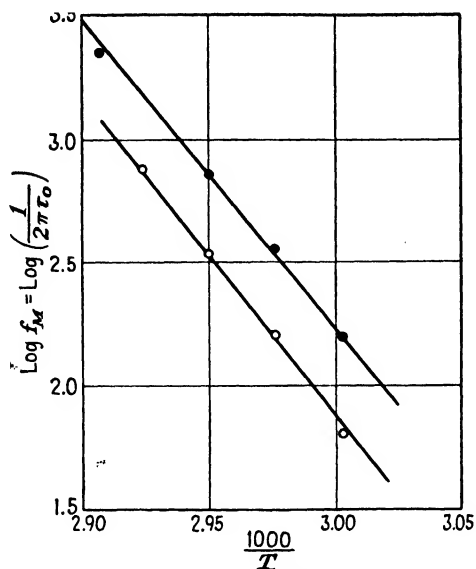


FIG. 10-10. Dependence of relaxation time on temperature for polyvinyl acetate. *Upper curve:* lower-molecular-weight material. *Lower curve:* higher-molecular-weight material. [D. J. Mead and R. M. Fuoss, *J. Am. Chem. Soc.*, **63**, 2832 (1941).]

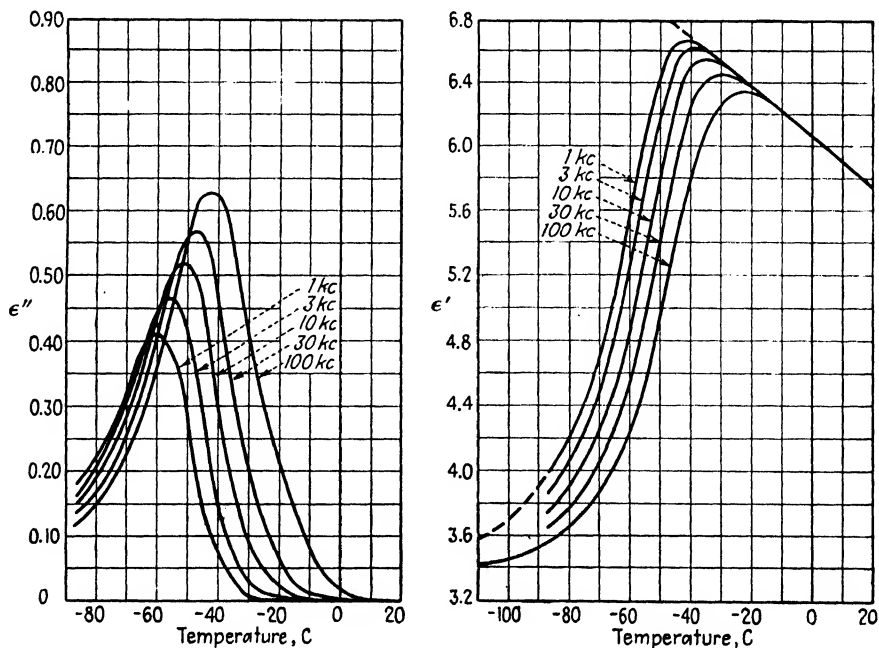


FIG. 10-11. Dielectric properties of halowax as a function of frequency and temperature. [S. O. Morgan, *Trans. Electrochem. Soc.*, **65**, 109 (1934).]

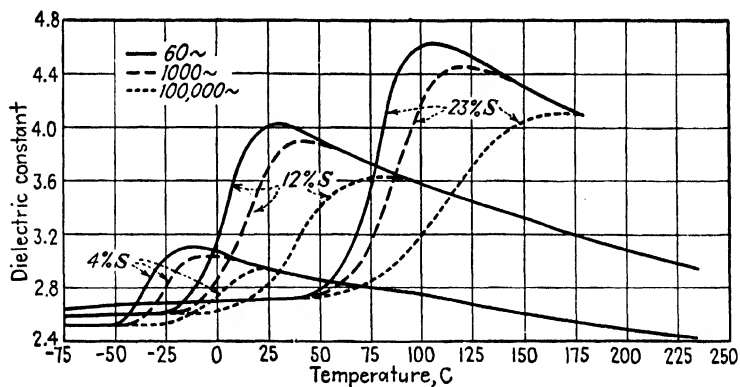


FIG. 10-12. Dielectric properties of a rubber vulcanizate as a function of frequency and temperature. [A. H. Scott, A. T. McPherson, and H. L. Curtis, *J. Research Nat. Bur. Standards*, **11**, 173 (1933).]

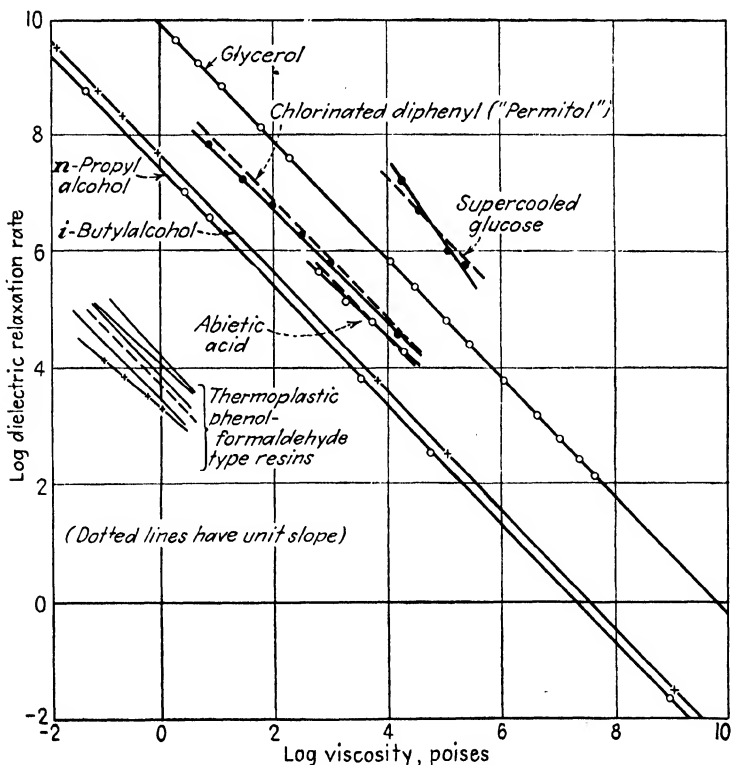


FIG. 10-13. Relationship between viscosity and dielectric relaxation. [W. Kauzmann, *Rev. Modern Phys.*, **14**, 12 (1942).]

1007. Low-loss Insulators. High-polymer products are widely used as electrical insulators. As Table 10-1 indicates, they have resistivities of so much higher an order than the metals—the resistivity of copper is 1.72×10^{-6} ohm-cm—that all are suitable for conventional d-c or 60-cycle a-c purposes, *e.g.* for plugs, switches, and housings. Choice is usually made on the basis of service conditions, cost, and mechanical shock resistance. For high voltages the dielectric strength, naturally, is an additional factor, and the choice is more limited. When flexibility is a requirement, rubbery materials must be used. Until comparatively recently, rubber was used almost exclusively for wire and cable insulation, except for submarine cable, where gutta-percha was superior because of greater resistance to water. For relatively short lengths of wire used in electrical devices, synthetic high-polymer products are now widely used, *e.g.*, polyvinyl formal, plasticized polyvinyl chloride, and silicone resins, because of a superiority to rubber in respect to one or more properties such as flame resistance, temperature stability, abrasion resistance, or solvent resistance.

Where good insulating properties are required but flexibility is not, the materials most widely used are hard rubber, polystyrene, phenolic laminates, aniline-formaldehyde resin, mica-filled phenolics, glass-bonded mica, and ceramics. Each has definite uses, advantages, and disadvantages. Thus, the organic materials cannot be used at high temperatures; the inorganic materials are brittle; hard rubber and the phenolics are affected by ultraviolet light and weather conditions; the ceramics and mica combinations are difficult to machine, and so on.

In a-c circuits, low dielectric constant and low loss factor are desirable to minimize power losses. In this regard, the organic high polymers as a class are superior to inorganic materials. Furthermore, the inorganic insulators, except for impervious materials such as glass and porcelain, are more often affected by water, which not only decreases volume and surface resistance (Secs. 1001 and 1002) but also increases dielectric constant and loss factor (Figs. 10-15 and 10-6).

Many high-polymer products that have found wide application in a-c equipment at low and medium frequencies by virtue of their low loss characteristics are unsatisfactory at higher frequencies such as 1 megacycle, owing to the appearance of a region of dielectric absorption. As expected, polymers without polar groups are superior to those with such groups (Table 10-1). In many cases a loss-factor increase is due to the filler rather than to the binder. Thus, phenolic molding compositions containing cellulosic fillers exhibit a loss-factor increase in the range 10^6 to 10^9 cycles, whereas substitution of mineral fillers for cellulose eliminates this peak (Table 10-1). In addition, the dielectric properties of mineral-

filled resins are much less moisture-sensitive than those of cellulose-filled resins.

Plasticized thermoplasts as a group are not satisfactory as high-frequency dielectrics. Thus, introduction of an ester plasticizer in a nonpolar polymer, *e.g.*, esters in polyvinyl chloride, introduces polar material with consequent increase in dielectric absorption (Fig. 10-14). Use of a nonpolar plasticizer in a polar polymer, *e.g.*, hydrocarbon oils in

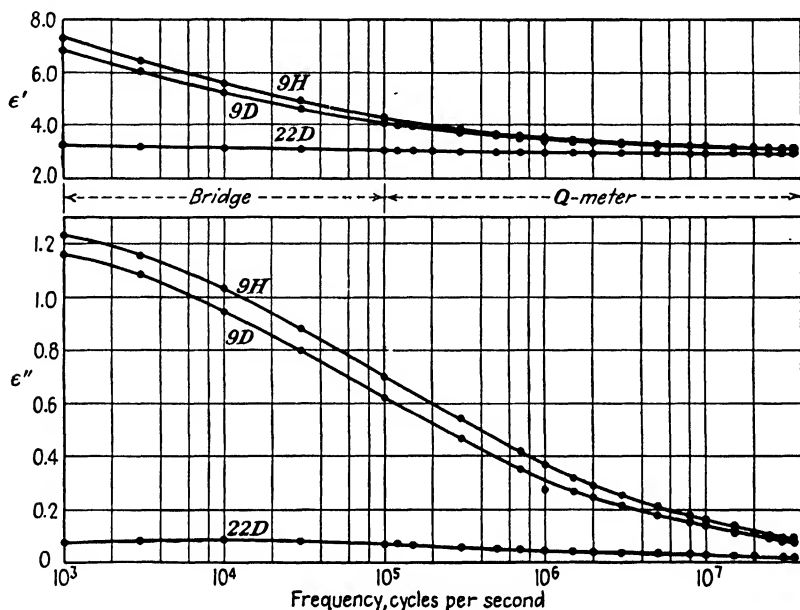


FIG. 10-14. Dielectric properties of polyvinyl chloride as a function of frequency. Curve 22D: unplasticized, dry. Curve 9D: highly plasticized, dry. Curve 9H: highly plasticized, humidified at 60 per cent relative humidity. [W. A. Yager, *Trans. Electrochem. Soc.*, **74**, 113 (1938).]

cellulose acetate, decreases the dipole losses but introduces interfacial polarization so that usually there is a net loss.

The advent of radio, television, radar, and similar devices in which high frequencies are used has made the development of very low loss dielectrics particularly important. Even a small amount of dielectric absorption results in serious loss over a long line. Thus the loss in the dielectric of a high-frequency coaxial cable transmission line is

$$A_d = K \sqrt{\epsilon} f \tan \delta \quad (10-14)$$

where A_d is the attenuation in power per unit length of line, K a constant, ϵ the dielectric constant, and $\tan \delta$ the dissipation (which equals the power factor for small values). Increasing the frequency from the range around

1 megacycle (AM radio spectrum) to 100 megacycles (FM radio spectrum) increases the attenuation in the line a hundredfold.

Since all high polymers otherwise suitable for dielectrics have fairly similar dielectric constants (ranging from 2 to 5), the important quantity in this equation is the power factor. Evidently decrease in power factor from 0.01 to 0.001 is a major gain, resulting in a tenfold decrease in attenuation. The great value of polyhydrocarbons as high-frequency transmission-line dielectrics is self-evident (Table 10-1).

The operation of communication devices involves transmission of signals with varying frequencies. Should a dielectric be used with a region of anomalous dispersion occurring in the frequency range employed, the losses would vary irregularly over that range—a result even worse than a steady high loss since, for example, it would change the quality of a transmitted voice. It is for this reason that polyvinyl chloride, ethyl cellulose, etc., cannot be used for insulation at high frequencies. That is, even when attenuation is not a factor, as in electronic devices other than transmission lines, polystyrene and similar dielectrics are chosen as insulators because of the constant power factor.

TABLE 10-2. EFFECT OF IMPURITIES ON DIELECTRICS

Material	Frequency, kc	Dielectric constant	Power factor	Resistivity $\times 10^{-18}$, ohm-cm
Gutta-percha, commercial.....	1	4.13	0.031	
Gutta-percha, dried.....	1	3.01	0.018	2.5
Gutta-percha, refined.....	1	2.78	0.0035	6
Gutta-percha, extracted.....	1	2.56	0.0009	37
Polystyrene, from regular styrene.....	3×10^6	0.00043	
Polystyrene, with 0.1 % catalyst.....	3×10^6	0.00049	
Polystyrene, with 0.1 % inhibitor.....	3×10^6	0.00051	
Polystyrene, from highly purified styrene, polymerized <i>in vacuo</i>	3×10^6	0.00017	

CURTIS, H. L., and A. T. MCPHERSON, *Nat. Bur. Standards Technol. Papers*, **19**, 669 (1925).
VON HIPPEL, A., and L. G. WESSON, *Ind. Eng. Chem.*, **38**, 1121 (1946).

From the chemical structure of hydrocarbon-type dielectrics, one should expect zero power factor, but this is never the case. It turns out that there is always a power factor due mostly if not entirely to polar-type impurities (Table 10-2). Synthetic polyhydrocarbons have lower power factors than commercial Hevea rubber and gutta-percha owing to the absence of proteins and other polar-type impurities. However, even with the synthetics there are large variations in power factor, owing to the presence of traces of inhibitor, catalyst, and water (Table 10-2).

Obviously, special precautions are necessary for the preparation of "electrical-grade" polymers.

1008. Dielectric Heating. The phenomenon of anomalous dispersion is the basis of dielectric heating (Sec. 834) of high-polymer products. The identification of the specific types of polarization occurring in these materials is usually difficult, owing to the many substances present in the mix, *e.g.*, monomers or early-stage resins, unreacted components, side and decomposition products of the reaction, catalysts, fillers, plasticizers,

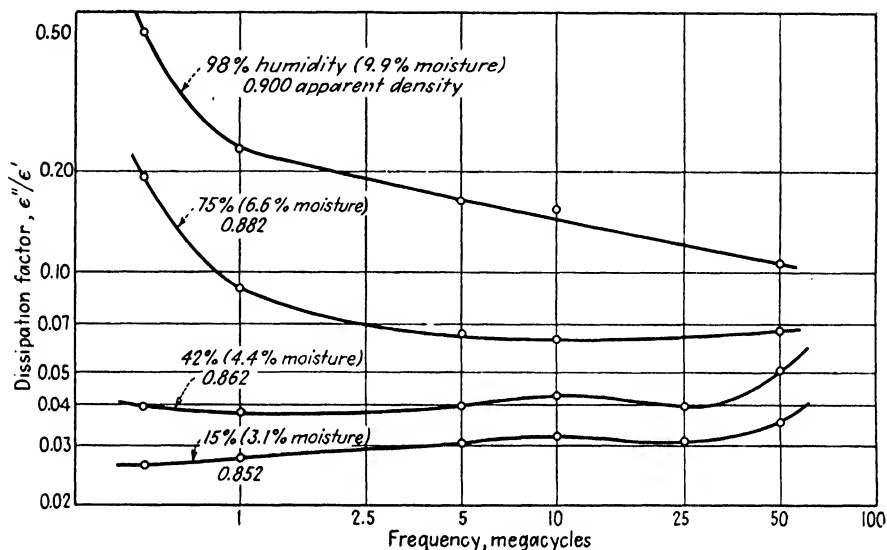


FIG. 10-15. Dielectric properties of a material as a function of frequency and humidity. Cellulose fabric impregnated with phenolic resin; temperature 28 C. [T. W. Dakin and R. W. Auxier, *Ind. Eng. Chem.*, **37**, 268 (1945).]

lubricants, and coloring materials. Obviously, polarizations will occur corresponding to each type of dipole present. In addition, since such mixes are almost always heterogeneous, interfacial polarizations will take place. Furthermore, conducting impurities are almost always present, imparting a d-c conductance and enhancing interfacial polarization (Fig. 10-6). Hence, it is evident that a region of dielectric absorption observed in such a system may be due to any one or a combination of several types of polarization. Flat loss-factor curves with broad peaks that extend over several decades of frequency are the rule (Fig. 10-14). Narrow-peaked curves are observed only in pure thermoplastics which undergo no change on heating (*e.g.*, in Fig. 10-9, note the great changes of loss factor with frequency at constant temperature). Consequently, it is extremely difficult to determine the precise mechanism of the dielectric absorption in any particular mix. Humidity is a major variable (Fig.

10-15), especially when cellulosic materials are present. For this reason and because of manufacturing variability in composition the dielectric-absorption properties of similar mixes may vary considerably.

At first thought, one might assume it desirable to carry out dielectric heating at the frequency corresponding to a loss-factor peak in order to attain the maximum heating effect. However, this assumption is generally incorrect. From Eqs. (10-9), (10-11), and (10-12), neglecting the usually negligible power consumed in ohmic conduction, the rate at which a dielectric absorbs energy from an applied alternating electric field is:

$$W = KE^2f\epsilon'' \quad (10-15)$$

where K is a constant. Evidently the product $f\epsilon''$, which may be designated as the *heating factor*, determines the heating rate rather than ϵ'' alone. Consequently, in most high-polymer mixes where the loss-factor maximum, if any, is broad, the heating factor hardly diminishes at all as the frequency increases beyond that of the loss-factor maximum (Fig. 10-16). It is thus evident that, as a general rule in high-polymer mixes, the higher the frequency, the more rapid the heat generation within the specimen for a given voltage.

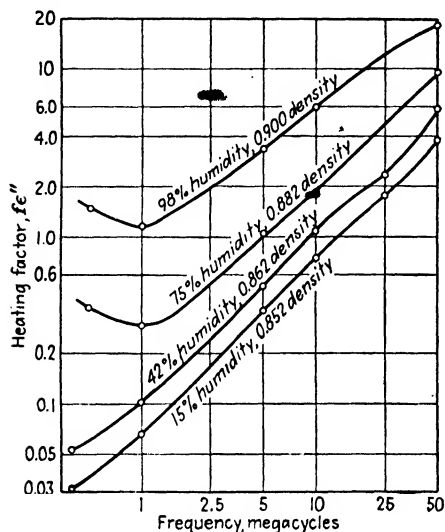


FIG. 10-16. Heating factor for a material as a function of frequency; same material and conditions as in Fig. 10-15. [T. W. Dakin and R. W. Auzier, *Ind. Eng. Chem.*, **37**, 268 (1945).]

This is of great practical importance, obviating the need of measuring loss-factor properties of the materials. However, there is a top limit to the usable frequency, *viz.*, that at which dipole polarization can no longer take place (Fig. 10-4). But it so happens that the limit is usually imposed by other considerations such as the availability of oscillators with appreciable power input at high frequencies or the size of the work, which determines tuning factors for the system. In practice, 30 megacycles is the top limit for articles of moderate size and 50 megacycles the limit for small articles.

It is evident from Eq. (10-15) that voltage gradient is a major factor in dielectric heating. This is limited in some cases by the flashover voltage of the electrode system and in others by the breakdown voltage of the material. Owing to the porosity of the materials being heated, the dielectric strengths are usually small, 25 volts per mil being a high value.

The manner in which the loss factor varies as the temperature rises is a major consideration in dielectric heating. Certain plastics, mainly of the thermoplastic group, tend to develop a "runaway" condition, resulting in overheating to temperatures above the decomposition point (Fig. 10-17). Obviously, careful control is imperative for such materials. Fortunately, thermosetting plastics in general do not exhibit this effect (Fig. 10-18), which accounts for the relative success that has attended the molding of these materials with high-frequency dielectric heating. As the temperature rises for the thermosetting materials, the dielectric

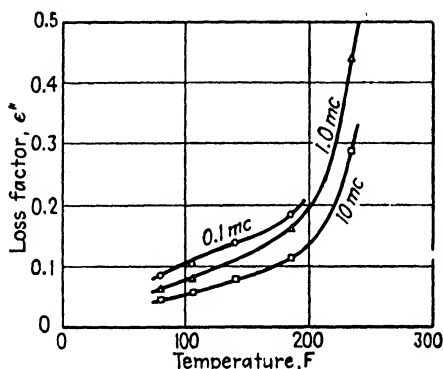


FIG. 10-17. Loss factor of a molded thermoplast as a function of frequency and temperature. [T. Hazen, *Trans. Electrochem. Soc.*, **90**, 263 (1946).]

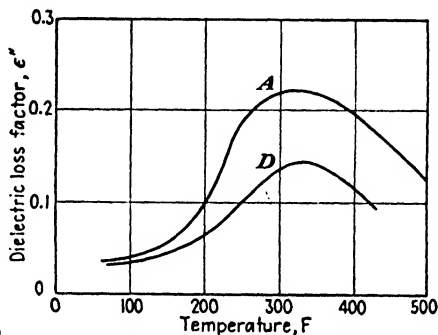


FIG. 10-18. Loss factor of thermosetting plastics as a function of temperature; frequency, 30 megacycles. Curve A: phenol-formaldehyde, no filler. Curve D: phenol-formaldehyde, mica filler. [T. Hazen, *Trans. Electrochem. Soc.*, **90**, 263 (1946).]

loss factor rises while the material enters and passes through the initial thermoplastic stages and then either decreases or tends to flatten off as the curing into the relatively infusible state takes place.

The temperature rise during dielectric heating is directly proportional to the power input [Eq. (10-15)] and inversely proportional to the specific heat of the material. However, such calculation of temperature rise is not very useful quantitatively in practice, because of voltage drops at the air gaps separating the electrodes from the material, variable voltages over the electrodes owing to tuning factors, heat variation of the loss factor with temperature, change of specific heat with temperature, heat losses by radiation and convection, heat absorbed in chemical reaction, and heat consumed in vaporization of volatile material. An additional complicating factor is the change of loss factor and specific heat due to chemical reaction. Nevertheless, approximations may be made in some cases. For example, with a short heating cycle the variation in loss factor and specific heat due to chemical reaction may be neglected, since

the chemical reaction does not proceed appreciably until the power input is nearly complete.

THERMAL PROPERTIES

The thermal properties of high polymers are often incidental to their application. However, in many instances, the limiting factor in application is the temperature the material will successfully withstand. The low thermal conductivity, especially of expanded materials, is responsible for some outstandingly successful applications as thermal insulators.

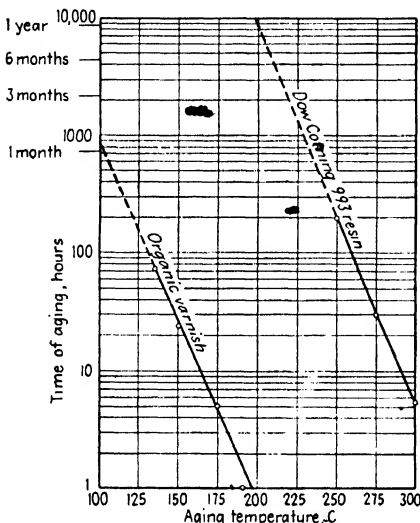


FIG. 10-19. Flexing life of varnishes. *Organic varnish*: phenolic-alkyd type. *Dow Corning resin*: silicone type. [S. L. Bass, M. J. Hunter, and T. A. Kauppi, *Trans. Electrochem. Soc.*, **90**, 311 (1946).]

figure and has no precise meaning unless the conditions of test correspond exactly with the conditions of use. However, generally speaking, most synthetic thermoplasts like the cellulose esters and ethers and the linear vinyl polymers will not withstand a continuous temperature of 100 C, whereas nylons, silicones, and space polymers like the phenolic, urea, and melamine resins will. (The boiling point of water is a particularly important temperature since it is often encountered in practice.) Fillers greatly influence heat resistance and may lower or raise it. Asbestos and glass fillers yield products of high heat resistance combined with good mechanical properties. Cold-molded refractories based on cement and clay withstand temperatures of 700 C; those made from mixtures of asbestos with asphalt or pitch and oil, 280 C.

The silicones as a class withstand temperatures at least 100 C higher on the average than comparable phenolics, ureas, and melamines.

1009. Heat Resistance. In considering a new fiber, rubber, or plastic, after having determined that the strength characteristics are satisfactory, the next question asked by the designer or prospective user is, "What is the maximum continuous operating temperature that the material will withstand?" Heat resistance is measured by the flow temperature, heat-distortion point, and other tests. "Maximum safe continuous operating temperature" is supposedly that temperature which the material will withstand without blistering, charring, distorting, or losing appreciably in strength or appearance. It is a highly arbitrary

Although inorganic cold-molded plastics are even more heat-resistant, their physical properties limit the applications. The excellent heat resistance of the silicones is utilized in electrical insulating varnishes and coatings (Fig. 10-19). They may be applied (1) to reduce size and weight of some apparatus through increase in operating temperatures, (2) to permit operation in high ambient temperatures, and (3) to obtain increased insulation service life or reliability where it is desired to maintain conventional size, weight, and temperature. As an illustration, in one test a motor operating at 300 C with insulation made of inorganic materials bonded and impregnated with silicone resin exhibited a service life about five hundred times as long as a similar motor operating at 200 C with the type of insulation previously used for high-temperature service.

1010. Thermal Conductivity. It can be shown theoretically that the thermal conductivity of metals is directly proportional to their electrical conductivity.

For the same molecular reasons that high polymers are electrical insulators, they are also thermal insulators (Table 10-3). In comparison with metals, plastics are comfortable to the touch when cold. Plastic handles are widely used on metal heating vessels such as cooking utensils.

In some cases it is desirable to increase the thermal conductivity of a plastic to improve heat dissipation. This may often be accomplished with suitable fillers; *e.g.*, mineral-filled phenolics have thermal conductivities three or four times that of unfilled and organic-filled phenolics. Thermal conductivity is one of the factors determining heat build-up in a cyclically stressed member.

1011. Thermal Expansion. The high thermal expansion (and shrinkage) of plastics (Table 10-4) is often a major disadvantage in their application. Thus it is a factor working against adhesion of organic surface coatings (Sec. 1417), and plastic-metal assemblies may present a problem because of unequal expansion and attendant buckling, cracking, or loosening. Rubber-metal combinations are less affected, owing to the extensibility of the elastomer. Plastic parts, particularly for aircraft, are frequently tested by chilling to -70°F and then heating to 120°F , often in a repeated cycle. This will cause failure in improperly molded or designed parts. Thermal expansion or contraction may throw a part out of tolerance, which is one reason why metals, with their lower coefficients, are suitable for machined parts with close tolerances where plastics are not.

The coefficient of expansion of an organic polymer is reduced on addition of inorganic fillers. Figure 10-20 shows the behavior of glass-polystyrene mixtures. The product, Polyglas, has special electrical applications.

TABLE 10-3. THERMAL INSULATING PROPERTIES OF MATERIALS

Material	Apparent specific gravity	Thermal conductivity, cal/sq cm sec (deg C/cm) $\times 10^4$
Metals.....		200-10,000
Aluminum.....	2.7	4,850
Steel.....	7.9	1,500
Cold-molded materials:		
Concrete.....	1.6-2.2	15-22
Brick.....	0.8-1.7	8-12
Organic.....	2	17
Organic plastics.....		2-16
Phenol-formaldehyde, inorganic fillers.....	1.6-2	8-16
Phenol-formaldehyde, organic fillers.....	1.3-1.5	4-7
Urea-formaldehyde.....	1.5	7
Ethylene.....	0.9	8
Nylon.....	1.1	6
Methyl methacrylate.....	1.2	4-6
Cellulose esters and ethers.....	1.1-1.5	3-8
Vinyl chloride plastics.....	1.2-1.6	3-4
Vinylidene chloride.....	1.7	2.2
Styrene.....	1.1	2
Rubbers.....		3-8
Hevea rubber, soft vulcanizate.....	1.1	3-8
Hevea rubber, hard vulcanizate.....	1.2	4
Woods (across grain).....		1-4
Spruce.....	0.4	2.6
Balsa.....	0.1	1.1
Fabricated materials in sheet and board form:		
Sugar-cane fiber (Celotex).....	0.2	1.2
Corkboard.....	0.1-0.2	0.9-1.2
Hair felt.....	0.2	0.9
Treated wood fiber (Balsam Wool).....	0.04	0.9
Kapok between burlap (Dry Zero).....	0.02-0.04	0.8
Aluminum foil, air laminate.....	0.004	1.0
Expanded materials:		
Gypsum, cellular.....	0.2-0.4	1.5-3
Rubbers, cellular.....	0.07-0.2	0.8-1.3
Cellulose acetate.....	0.06-0.2	1.0-1.2
Phenolic resin.....	0.03-0.2	0.9-1.1
Polystyrene.....	0.03-0.1	0.8-1.1
Glass, cellular.....	0.17	1.5
Loose materials:		
Steel wool.....	0.08-0.15	2
Sawdust.....	0.2	1.2-1.4
Diatomaceous earth.....	0.2	1.1
Cork.....	0.15	1.0-1.1
Mineral and glass wool.....	0.1-0.3	0.9-1.2
Kapok.....	0.015-0.03	0.8-1.2

Data from various sources, notably

PERRY, J. H., editor, "Chemical Engineers' Handbook," 2d ed., McGraw-Hill Book Company, Inc., New York, 1941.

PLASTIC MATERIALS MANUFACTURERS' ASSOCIATION, "Technical Data on Plastics," Washington, D.C., 1945.

TABLE 10-4. THERMAL EXPANSION OF MATERIALS
(Room temperature)

Material	Linear Coefficient $\times 10^5$ per deg C
Glass and ceramics.....	0.1-1
Vitreous silica.....	0.1
Pyrex laboratory glass.....	0.3
Optical glasses.....	0.8
Vitreous enamels.....	1-3
Metals.....	0.5-3
Steel.....	1.2
Brass.....	1.9
Aluminum.....	2.4
Organic thermoset plastics.....	2-5
Phenol-formaldehyde, wood-flour-filled.....	3
Urea-formaldehyde.....	3
Casein plastic.....	5
Wood:	
Parallel to grain.....	0.2-0.6
Across grain.....	2-6
Hevea rubber, hard vulcanizate.....	8
Organic thermoplastics.....	6-20
Styrene.....	7
Methyl methacrylate.....	8
Nylon.....	10
Cellulose esters and ethers.....	6-17
Ethylene.....	17
Vinylidene chloride.....	19

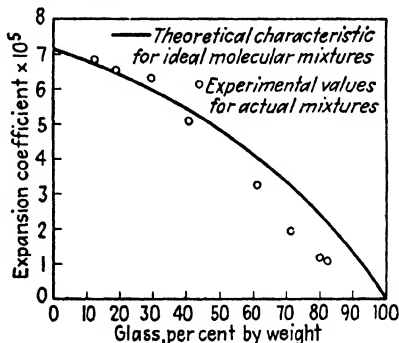
Data from various sources, mainly

PLASTIC MATERIALS MANUFACTURERS' ASSOCIATION, "Technical Data on Plastics," Washington, D.C., 1945.

"International Critical Tables," McGraw-Hill Book Company, Inc., New York.

Over a large range of temperature the *change* of coefficient of thermal expansion with temperature must be considered. All materials exhibit an increase in the coefficient with temperature; *e.g.*, aluminum has the value 1.8×10^{-5} per deg C at -75°C and the value 2.5×10^{-5} at 75°C ; methacrylate plastic has the value 6×10^{-5} at -75°C and the value 11×10^{-5} at 75°C .

The intrinsic shrinkage that many plastics undergo after molding, particularly when heated (Secs. 818 and 927), complicates the effect of temperature rise.

FIG. 10-20. Thermal expansion of glass-polystyrene mixtures. [A. van Hippel and L. G. Wesson, *Ind. Eng. Chem.* **38**, 1121 (1946).]

OPTICAL PROPERTIES

1012. It will be recalled that when a beam of ordinary white light which has been traveling through air strikes the surface of a material, part is always reflected and the balance enters the material. Of the portion that enters, either all is absorbed, or part is absorbed and another part transmitted. Most commonly, the absorbed light degenerates into heat.

Like electrical and thermal properties, optical properties depend on the molecular, atomic, ionic, and electronic constitution. The size and vibration frequencies of the larger units are such that their effects are mainly on longer waves, whereas in the visible spectrum, with which we are mainly concerned, it is the concentration and mobility of the electrons that are of paramount importance. In view of the latter fact it follows that electrical, thermal, and optical properties are interrelated.

1013. Behavior of Metallic Crystals. In a typical metallic crystal (Sec. 206) there is a cloud or gas of highly mobile electrons. Owing to their presence, when light strikes a metallic crystal a large part of it is reflected. Metals owe their characteristic luster to this intense reflection power. Polished silver may reflect 90 per cent of the light that falls upon it, while glass reflects about 5 per cent at perpendicular incidence.

White light reflected from a colored nonmetallic solid like red or blue glass remains white, but when reflected from copper it is red. That is, the reflection of visible frequencies from some metals is selective, some being reflected more strongly than others, accounting for color.

What little light enters a metal is rapidly absorbed. The electrons are so mobile that they are readily displaced, and the energy of entering photons is transferred to them, regardless of frequency. (Indeed, the actual expulsion of electrons excited by ultraviolet light gives rise to the well-known photoelectric effect.) As a consequence, the beam is completely extinguished; metals are invariably opaque in thicknesses greater than a few atomic layers.

1014. Behavior of Nonmetallic Crystals. In crystals where the primary bonding is other than metallic, *i.e.*, ionic, covalent, or coordinate, the electrons are far less mobile. The quanta of visible light cannot cause electron flow. They can only modify the vibration about mean equilibrium positions. Reflection and absorption are much less marked. Hence the general tendency is toward transparency. It is thus seen that the transmission of light (transparency) takes place most readily in electrical insulators, and vice versa. It is therefore impossible for a transparent material to be a good electrical conductor, or vice versa.

Semimetallic (metalloidal) crystals contain metallic atoms and atoms

of the sulfur and arsenic groups. The bonding is partly metallic, partly nonmetallic. Their optical and electrical properties are of an intermediate nature.

1015. Interrelation of Mechanical, Electrical, Thermal, and Optical Properties. Surface hardness and mechanical properties, which are important determinants of the applicability of optical materials, dielectrics, and thermal insulators, are, of course, also dependent upon the type of bonding in the crystal. The state of affairs is shown in Fig. 10-21, which correlates mechanical, electrical, thermal, and optical properties

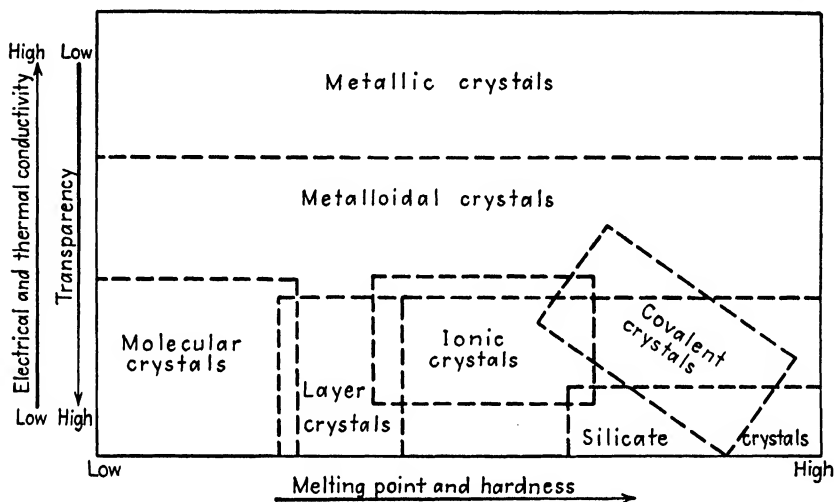


FIG. 10-21. Properties of different crystal types. (H. G. Deming, "General Chemistry," John Wiley & Sons, Inc., 1935. Reproduced by permission.)

from a broad viewpoint. As a group, organic high polymers are bridged by secondary valence forces and fall into the lower left-hand corner of the figure with other molecular crystals. They are insulators, many of which are highly transparent; but their melting points, surface hardness, and dimensional stability are comparatively low. Silicates as a class are not only transparent and nonconductive but hard and dimensionally stable as well. They withstand much higher operating temperatures and are not scratched easily. The implications so far as the manufacture of lenses and insulators is concerned are obvious. The significance of the silicones lies in the fact that they are organosilicate hybrids combining desirable properties of both classes to an intermediate degree.

1016. Color in Organic Compounds. The transmission of light through a material is always accompanied by a certain amount of absorption. In other words, every substance has an absorption spectrum. A material that is commonly termed "transparent" is merely one that

transmits without appreciable absorption part or all of the light in the visible spectrum. It generally exercises powerful absorptions in the infrared and ultraviolet regions. If the absorption in the visible spectrum is not particularly selective, the material is both transparent and colorless; otherwise, it is colored. The general absorption in the infrared region attributable to atoms and larger groups will be disregarded in the ensuing discussion.

In completely saturated aliphatic compounds, all the electrons are tightly bound, and hence a large amount of energy is required to raise a molecule to an excited state. Hence, such substances absorb only in the ultraviolet region and are generally colorless. If unsaturated linkages such as —C=C— , —C=O , —N=N— , —N=O , etc., are present, the less firmly bound unsaturation electrons require less energy to undergo a transition and absorption often takes place at lower frequencies, usually in the near-violet, more rarely in the visible spectrum. Color is not common. However, when two or more unsaturated bonds are present, the effect is often enhanced. This is especially true when double bonds are conjugated. In such structures, certain electrons are still more mobile, and the energy for electronic transition or excitation is so low that absorption in the visible spectrum (and hence color) is common. The so-called "chromophoric" groups of dyes are often conjugated structures.

Optimum colorability is attainable in plastic products only when the binder is colorless and transparent. When this is the case, any transparent or opaque shade may be produced by the introduction of appropriate dyes and pigments. Any color or lack of transparency in the binder imposes limitations.

1017. Refraction and Reflection. It is essential to recall some simple physical facts. When light meets an interface between transparent materials, part is reflected and part is refracted in accordance with the relative speeds with which the light travels in the two media. The index of refraction of a material is defined as

$$n = \frac{u_a}{u_x} = \frac{\sin i}{\sin r} \quad (10-16)$$

where u_a and u_x are the speeds of light in air and the material in question and i and r are the angles of incidence and refraction, respectively.

When an oblique beam passes from a less to a more optically dense medium, it is refracted toward the normal to the interface. For perpendicular incidence Fresnel has shown that

$$R = \frac{(n_2 - n_1)^2}{(n_2 + n_1)^2} \quad (10-17)$$

where R is the reflection coefficient, or fractional part of the incident light that is reflected, and n_1 and n_2 the respective refractive indexes of material 1 immersed in material 2 (both materials nonmetallic). When one of the two media is air, this reduces to

$$R = \frac{(n - 1)^2}{(n + 1)^2} \quad (10-18)$$

Refractive indexes of various transparent polymers are listed in Table 10-5.

TABLE 10-5. OPTICAL PROPERTIES OF TRANSPARENT PLASTICS
(Rigid grades)

Material	Specific gravity	Refractive index	Rockwell hardness	Aging characteristics (transparency before and after long-time exposure to "normal" light and atmosphere)			
				Light transmission, %		Haze value,* %	
				Originally	After 1 year	Originally	After 1 year
Methyl methacrylate.	1.19	1.49	M60-M100	94	93	2	3
Allyl resin, CR-39-1...	1.32	1.50	M95-M100	92	91	2	
Cellulose acetate.....	1.30	1.49	R105-R115	87	80	5	8-28
Cellulose acetate-butyrate.....	1.20	1.47	M25-M70	89	89	8	8
Cellulose nitrate.....	1.38	1.50	R90-R120	88	38	5	97
Ethyl cellulose.....	1.17	1.47	R50-R110	89	Very low	5-12	Very high
Vinyl chloride-acetate	1.34	1.52	83	83	7	7
Vinyl butyral.....	1.15	1.48	71	10	5	99
Polystyrene.....	1.06	1.60	M80-M90	90			
Cast phenolic.....	1.32	1.60	M20-M75	85			
Diamond.....	3.51	2.42	(10, Moh)†	Aging has no effect Aging effects are slight			
Plate glass.....	2.50	1.52	(5, Moh)†				

Data taken from various sources, notably

PLASTIC MATERIALS MANUFACTURERS' ASSOCIATION, "Technical Data on Plastics," Washington, D.C., 1945.

LARION, W. S., *Product Eng.*, **15**, 605 (1944).

* Haze value is the fraction of light scattered by diffusion. A perfectly transparent material would have a light transmission of 100 per cent and a haze value of zero. See A.S.T.M. Standard D 672.

† The hardness and scratch resistance of diamond and glass are so vastly superior to that of the organoplastics that they are not expressible in comparable terms.

If a beam of light starts in a material of high refractive index and meets an interface with air, part is again reflected and part is refracted

but this time the refracted beam is bent away from the normal. There is a critical angle for the incident beam at which it is refracted just parallel with the surface. At any angle greater than this, none of the original beam escapes to the air; all the light is internally reflected (Fig. 10-22). It may be shown that the sine of the critical angle, ϕ , is the reciprocal of the refractive index,

$$\sin \phi = \frac{1}{n} \quad (10-19)$$

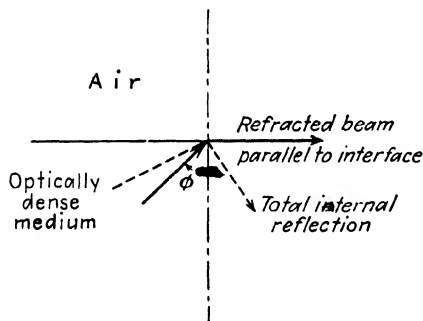


FIG. 10-22. Internal reflection.

1018. Effects of Surface Condition. Reflection from a smooth surface takes place in regular fashion and is called *regular* or *specular reflection*. None of the light seems to come from the surface itself; rather, it appears to originate behind the surface. A

surface must be plane to within a fraction of a wave length of the impinging light to get absolutely specular reflection. This is attainable only with great difficulty in practice; but, the more highly we can polish a surface, the more nearly specular the reflection and the more nearly invisible the surface.

By contrast, a rough surface scatters what light it reflects in the form of diffuse reflection, and the surface itself is readily visible. Thus, a massive crystal of transparent colorless material changes its appearance to that of a translucent or even opaque white mass when ground to a sufficiently fine powder. Again, a dark-blue transparent crystal becomes whitish blue and opaque on grinding because the light reaching the eye is a mixture of blue transmitted light and large amounts of diffusely reflected white light. The effects of uneven surface are thus twofold, a loss of transparency and a large gain in diffuse reflection.

Equation (10-18) states that a transparent solid of high refractive index with highly polished faces reflects incident light rather intensely. Equation (10-19) states that light which has entered such a solid may undergo considerable internal reflection before it escapes. This accounts for the brilliance of precious gems, which are scratch-resistant polished stones of high transparency and high refractive index, *e.g.*, diamond (Table 10-5). Freedom from light-scattering flaws, bubbles, grains, etc., is of prime importance, as is a surface that not only can be polished to exceptional smoothness but also is hard enough to resist marring. The problems involved in simulating such gems with transparent organic high polymers are thus indicated. Their refractive indexes are of the order of 1.45 to

1.65, about the same as glass. Transparency of a high degree is attainable, notably with the acrylics, but scratch resistance is of a low order.

Gloss, or *luster*, is the ability to reflect large amounts of light by specular reflection. Smoothness and homogeneity of surface and refractive index are the main determinants of this property.

Equation (10-17) shows that if a material is surrounded by another of equal refractive index no light will be reflected. Thus, in an emulsion of two colorless liquids of equal refractive index the dispersed droplets cannot be seen. However, as the difference in refractive index between two media is broadened, more light is reflected. How this important property is controlled in synthetic fibers and gloss paints is discussed in Secs. 831, 1421, and 1428.

Lightness (less correctly, brightness) is the ability to reflect light diffusely. It is a key property in flat paints for home and business interiors. A high intensity of diffuse lighting may be obtained from a paint film by incorporating light-colored pigments of high refractive index in amounts sufficient to prevent the formation of a smooth film surface. The control of lightness and hiding power is discussed in Sec. 1428.

1019. Birefringence and Polarization. The velocity of light through a medium depends on the optical density of the medium, which in turn is determined by the number and mobility of the electrons. It will be recalled that, in all crystals other than those belonging to the regular or cubic system, the optical density is different for different axes so that they manifest to a greater or lesser degree the phenomenon of *double refraction*, or *birefringence*. When a beam of unpolarized light is passed through, two refracted beams emerge instead of one. These two beams are found to be polarized at right angles to each other. Owing to the lack of molecular arrangement, liquids are nonbirefringent.

It follows from the above that a crystalline oriented element of a high-polymeric substance will exhibit birefringence and the ability to polarize light. This is inherent in the long-chain character of the molecules. However, an unoriented amorphous element will be nonbirefringent like a liquid. This is often a useful method for determining high-polymer structure (Fig. 2-11, page 57).

If chain molecules are dissolved in a low-molecular-weight solvent, the resulting solution is nonbirefringent, as expected. However, it is often found that, if the solution is caused to flow at velocities such that turbulence is avoided, it becomes birefringent (Sec. 628). This phenomenon is known as *stream birefringence*. It is also manifested by some colloidal dispersions of solid particles. If the velocity of flow is increased to the point of turbulence, nonbirefringence results. It may be safely

concluded that stream birefringence is a manifestation of flow-induced preferential alignment of the solute. This serves to detect the cause of various thixotropic behaviors of high-polymeric and colloidal dispersions (Secs. 719 ff.).

It has been found that films of high-polymeric materials, notably polyvinyl alcohol, $-(\text{CH}_2\text{CHOH})_n-$, in which the molecules have been highly aligned by drawing, may be used to polarize light. Crossed films, like crossed tourmaline crystals, extinguish a light beam. Polaroid glasses may be made by interleaving a layer of the oriented film between two layers of glass, much as in safety-glass construction. It is claimed that they are more transparent and less expensive to make than previous polarizing units. Moreover, there are no limitations as to size or shape, as there are for natural crystals.

1020. Stability of Optical Properties. We shall define *optical stability* as the ability of an artifact to maintain its original optical properties during its service life. Obviously, this property may be just as important as the original optical properties.

Both mechanical and chemical properties influence the optical stability in the sense here employed. For example, chemical decompositions or transformations may cause changes in color and transparency; cracking, scratching, or wrinkling of the surface alters gloss and light transmission and causes distortion of transmitted vision; creep alters the focal length of a lens.

Many transparent high polymers deteriorate optically on normal exposure to the atmosphere. Light absorption may increase or haziness may develop owing to reactions with oxygen, the absorption of moisture, the elimination of decomposition products, or the formation of cracks on or under the surface. This deterioration is loosely described as aging. Fundamentally, it resolves itself mainly into terms of reactions with light, oxygen, and water.

The high-frequency components of light are usually most active in causing photochemical deterioration. Aging may be hastened by metallic impurities and catalysts left in the product. It may be accelerated or retarded by different dyes, pigments, or plasticizers. It follows that compounding ingredients must be chosen carefully as to kind and amount whenever optical properties are of paramount importance. The superiority of polymethyl methacrylate as a transparent plastic lies as much (if not more) in its relative resistance to aging as in its superior light transmission.

1021. Window Material. For members such as flat and curved windows, instrument dial faces, etc., the transparent plastics must compete with glass. Polymethyl methacrylate may be selected as the representative of organic high polymers and compared with glass as follows:

Its advantages are that it has low specific gravity, is nonshattering, has high shock resistance, high light transmission, and low haze value, produces little distortion of vision, has relatively high ultraviolet-light transmission, and is easy to produce in the form of large, thick members of intricate curvature.

Its disadvantages are its very low scratch resistance and comparatively low optical stability.

The very low scratch resistance compared with glass is the curse of transparent organic plastics. Yet windows, dial faces, and large, curved, transparent noses, blisters, and cockpit enclosures of American military planes of the Second World War were made of polymethyl methacrylate. The specific gravity, 1.19, is less than half that of glass, permitting a substantial saving in weight. It is nonshattering. Glass shatters under the impact of a projectile into sharp, daggerlike shards that endanger eyesight or even life. This does not happen with the plastic. Owing to low shock resistance, glass members break if a plane is set down hard. Flying shards not only endanger the passenger but might ruin many instruments. From a production standpoint, the manufacture of large, thick, intricately curved glass members is extremely difficult if not impossible. These same members are readily cast from plastics or even made from flat stock by heating in an oven, draping over a form, and allowing to cool and set to shape.

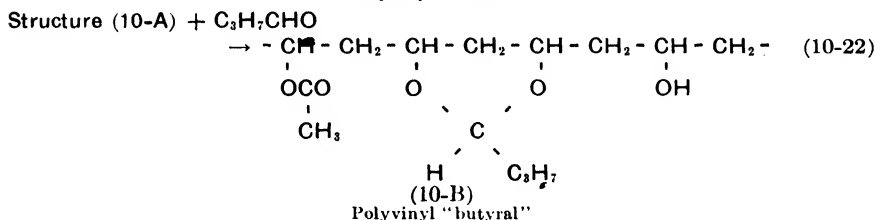
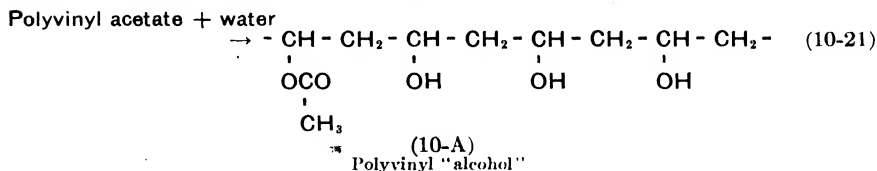
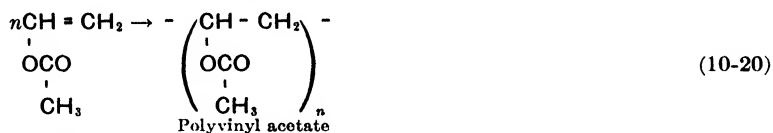
Unlike glass, sufficient ultraviolet light is transmitted by ordinary polymethyl methacrylate so that a person may become sun-tanned behind windows of this material. For transparent aircraft members it has been found necessary to produce a special ultraviolet-absorbing acrylic resin to prevent overexposure.

1022. Safety Glass. A sandwich composed of two outer layers of glass bonded to a thin interlayer of tough transparent plastic serves as safety glass. When it is struck a sharp blow, the glass layers shatter as usual but the shards adhere tightly to the interlayer instead of flying. Safety glass thus combines the scratch resistance of glass with the safety of transparent plastic. It is made by laying up the plastic and carefully cleaned layers of glass in a press and applying pressure and mild heat to expel air and enhance adhesion.

The main criteria of quality for a safety-glass lamination are (1) strong adhesion to glass, (2) high toughness and impact strength that are maintained at the lowest and highest temperatures encountered in use, (3) high resistance to deterioration by light so that discoloration and hazing will not occur, (4) stability to air and moisture such that special sealing of the sandwich at its edges is not necessary, and (5) reasonably good light transmission.

Of the various plastics that have been used for this purpose, polyvinyl

butyral is outstanding. Like all polyvinyl acetals, it is made from polyvinyl alcohol, which, in turn, must be produced indirectly from polyvinyl acetate since vinyl alcohol monomer is nonexistent.



It is seen that the reactions may be controlled to yield greater or lesser proportions of acetyl, hydroxyl, and acetal units in the final product. The molecular symmetry is of such a low order that the polymer possesses rubbery stretch and exceptional toughness, which is maintained at low temperatures to a considerable extent. There are sufficient polar groups to ensure excellent adhesion to glass.

The interlayer does not discolor and is such that edge sealing of the safety-glass sandwich is not required—a tremendous advantage in production.

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See also Appendix A.

PARTICULAR TOPICS

See references accompanying tables and figures of this chapter.

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Dielectrics

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CHAPTER 11

FIBERS AND FIBROUS PRODUCTS

1100. Plants and animals, including man, use fibrous materials to manufacture clothing, paper, felt, rope, webbing, nets, and other structural members. The sheep and the seal grow protective clothing in the form of wool and fur. Man must manufacture his clothing and has found that spun products are superior to natural pelts for this purpose. The spider pastes one point of a mass of spinning solution to a beam or branch and then casts himself into space, relying upon the life line that he extrudes and cold-draws through anatomical spinnerets to save himself from crashing. The wasp is a papermaker, matting natural fibers into a crepe-paper home. Trees build stress-bearing members such as trunks, branches, and stems out of lignin binder and cellulose-fiber filler. Until the twentieth century, only natural fibers existed. In the twentieth century, man has made a remarkable advance by learning the art of manufacturing artificial and synthetic fibers.

The fiber industries represent a large part of the world's total commerce. One branch alone, the textile industry, is exceeded in value of output only by the food industry. In other words, first man must be fed, and second he must be clothed.

DEFINITIONS

1101. A fiber is a fine single filament. The immediately obvious characteristic of all fibers is tiny cross section coupled with comparatively great length. By A.S.T.M. definition, the ratio of length to diameter is at least 100.

Threads, yarns, strings, cords, and ropes are larger structures made by combing, drafting, or otherwise manipulating large numbers of fibers into parallel arrangement and then imparting sufficient twist to hold the assembly together as a cohesive whole. Larger items like cords and ropes are usually made by first assembling fibers into yarns and in turn assembling the latter into the larger unit.

A cloth is a pliable fabric made by weaving, knitting, or felting (Fig. 11-1). *Weaving* is the interlacing of two sets of yarns, the warp and the filling, at right angles. Strictly speaking, only woven goods should be called textiles. *Knitting* is the interlooping of yarn, one row of loops being caught into the previous row. *Felting* is the intertangling and

massing of *fibers* into a continuous, more or less dense mat. Woven and knitted goods have as their basic structural element the yarn, which is mechanically arranged in orderly fashion. By contrast, the basic element of a true felt is the fiber, and the structure is characterized by comparative disorder. Under the above definitions, papers and leathers are felts.

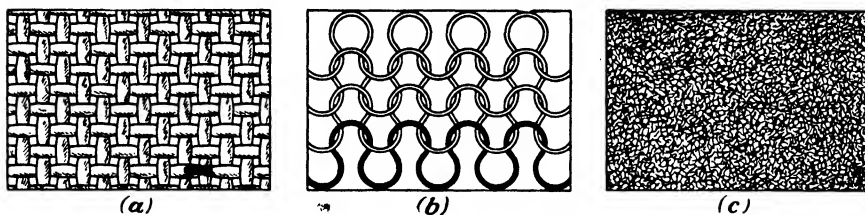


FIG. 11-1. Construction of fabrics. (a) Plain woven fabric. (b) Plain knitted fabric. (c) Felt.

FIBERS

1102. The fiber is a microbeam. The crux of the textile art is to assemble millions of these microbeams into large useful structures such as yarns, ropes, nets, and cloths in such a way that strength and toughness are achieved while the freedom and individuality of the microbeams and hence the inherent suppleness of the assembly are essentially preserved.

1103. Classification. Fibers are conveniently classified into three groups; natural, artificial, and synthetic.

An *artificial fiber* is one made by chemically modifying a *naturally occurring* high polymer. Typical of the artificial fibers are the rayons. The insoluble natural polymer, cellulose, is first converted into a soluble derivative such as cellulose xanthate or cellulose acetate, which is then spun into fibers. Other examples are the casein fibers. The first artificial fibers were developed around 1900.

A *synthetic fiber* is one produced by polymerizing man-made monomers to a suitably high level and then manipulating the resulting chain molecules into a typical fiber by any one of the spinning methods described in Secs. 830 ff.

Fibers may also be classified into thermoplasts and nonthermoplasts. The former, when sufficiently heated, fuse and exhibit continuous flow under pressure and can be dissolved in appropriate solvents. Examples are cellulose acetate rayon, nylon, polyvinyl chloride-acetate, Fiberglas, and polyvinylidene-vinyl chloride. The nonthermoplastic fibers decompose before they reach a temperature sufficiently high to exhibit plastic flow and cannot be dissolved by solvents. All natural cellulosic fibers fall into this group, together with viscose and cuprammonium rayons, which are regenerated celluloses; so also do wool and asbestos.

The main constituent of all natural fibers of vegetable origin is cellulose, a polyalcohol, while the animal fibers are proteins, natural polyamides. Indeed, all natural fibers are composed of very strongly polar molecules. The same is not true of artificial and synthetic fibers. Here the polarities vary over a much wider range. As a consequence, there is a greater range of properties than is found among the natural fibers.

1104. Structure. The structural features found in fibers are listed below according to size levels:

1. Atoms joined into mers
2. Mers joined into high-polymer chains

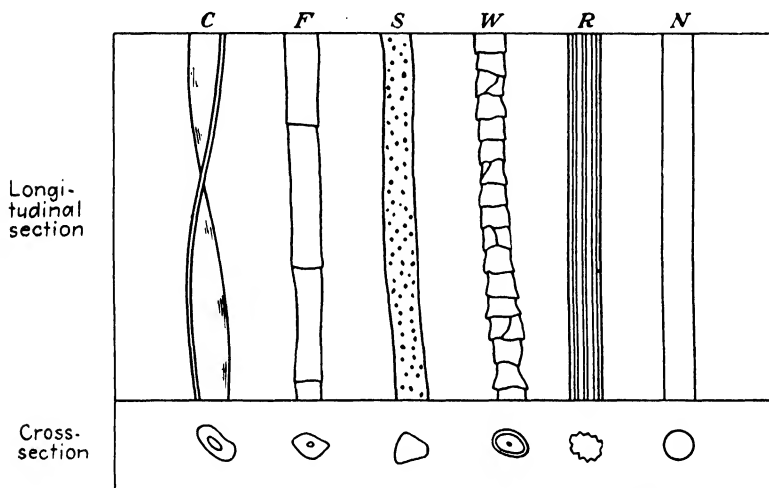


FIG. 11-2. Schematic features of some fibers as seen under the microscope ($\times 500$). C: cotton. F: flax. S: silk. W: wool. R: viscose rayon (bright). N: nylon. Glass and some other synthetic fibers exhibit the regular cylindrical structure of nylon. Actual photomicrographs as well as other identifying characteristics of fibers are given in (1) Am. Soc. Testing Materials Standard D 276. (2) (W. von Bergen and W. Krauss, "Textile Fiber Atlas," American Wool Handbook Co., New York.)

3. Chain molecules arranged into crystallites and amorphous regions with a preferential alignment along the fiber axis
4. Crystallites and amorphous regions joined and preferentially aligned in larger units called *fibrils*
5. Fibrils aligned preferentially along the main fiber axis
6. Fibers differentiated into cuticle, primary wall, secondary wall, central canal, or lumen, surface scales, etc.
7. Entire fibers spiraled or crimped

In some natural fibers the fibrils are prominent enough to be seen readily with an ordinary microscope (Fig. 5-34a, page 207). The same cannot be said for man-made fibers, and for a long while it was assumed

that fibrillar organization was absent from them. However, in 1946 it was discovered that rayons having a high order of crystallite orientation separate into fibrils under the action of appropriate chemical agents or mechanical treatment, whereas unoriented rayons show no evidence of fibrillation. It may therefore be said that structural features 1, 2, and 3 are common to all fibers, features 4 and 5 are common to all natural and some man-made fibers, while features 6 and 7 are practically unique to natural fibers. It follows that man-made fibers are, generally speaking, more uniform, less highly differentiated structures than natural fibers. Features of the gross organization of some fibers are shown in Fig. 11-2. The gross structures of cotton, wool, and silk were discussed in some detail in Secs. 504 *ff.* and those of wood in Sec. 937. The greatest single difference between natural and man-made fibers is that the former possess types of gross organization (features 6 and 7) that the latter do not. One may deduce the potential importance of this fact from the following examples.

1. The excellent felting properties of wool are at least partly traceable to epidermal scales protruding from the fibers. (So, for that matter, is the not so excellent scratchiness of some wool garments.)

2. The success of the papermaking process rests on the opening out of the cellulose fiber into hundreds of very fine fibrils during mechanical mauling in a suitable swelling agent (Sec. 1128).

3. The considerable differences between cotton and linen, two fibers consisting essentially of cellulose molecules, are mainly attributable to different fibrillar arrangement (Sec. 525).

Owing to the marked fibrillar character and the frequently present central canals, natural fibers are generally, though not always, more highly expanded materials than man-made fibers. Put another way, a natural fiber is more typically a porous tube, while a man-made fiber is usually a dense, nonporous rod. Some dyes, like the substantive, acid, and basic dyes, react chemically with the fiber. Others, like insoluble dyes, are held mechanically in pores. All dyes must penetrate the fiber to be effective, even, and fast. The dyeing of man-made fibers *per se* or the uniform dyeing of blends of man-made and natural fibers often presents a difficult problem.

Water-vapor and air transmission, water absorption, and thermal insulating properties are likewise greatly influenced by features of the gross organization.

1105. Tabulation of Fiber Characteristics. The most important characteristics of a fiber are summarized in Table 11-1. Many but not all of these will be discussed and related to production problems, application, and quality.

TABLE 11-1. IMPORTANT FIBER CHARACTERISTICS

Attributes of form and dimension	Physical and mechanical properties	Chemical properties
1. Length <i>a.</i> Average length <i>b.</i> Length distribution 2. Cross section <i>a.</i> Total area <i>b.</i> Uniformity <i>c.</i> Shape 3. Spiralilty 4. Crimp <i>a.</i> Frequency <i>b.</i> Amplitude 5. Surface character	1. Color 2. Luster 3. Refractive index 4. Specific heat 5. Conductivity <i>a.</i> Thermal <i>b.</i> Electrical 6. Softening or scorching temperature 7. Specific gravity 8. Mechanical properties <i>a.</i> Tensile strength <i>b.</i> Extensibility <i>c.</i> Stiffness <i>d.</i> Toughness <i>e.</i> Elasticity <i>f.</i> Resilience	1. Behavior toward moisture <i>a.</i> Moisture regain <i>b.</i> Swelling <i>c.</i> Drying 2. Behavior toward organic solvents 3. Resistance to heat 4. Resistance to atmospheric agents <i>a.</i> Oxygen <i>b.</i> Light 5. Behavior toward <i>a.</i> Acids <i>b.</i> Alkalies <i>c.</i> Dyestuffs

1106. Attributes of Form and Dimension. The contributions of form factors to the mechanical behavior of structural members have been indicated in Chap. 9. They are of immediate importance in the manipulation and production of fiber products as well as in respect to their final quality. Owing to preferential alignment of chain molecules, fibrils, or both, it goes without saying that fibers are highly anisotropic and lacking in strength balance.

1107. Fiber Length. Synthetic and artificial fibers may all be produced as continuous filament; but with the exception of silk, natural fibers come in comparatively short *staple lengths*. Thus, depending on the plant species, region of growth, climatic conditions, etc., cotton fibers are 0.5 to 2 in. long; depending on animal breed and age, climate, forage, etc., wool fibers may be 2 to 16 in. long (Appendix B).

To make a yarn out of continuous filaments is a comparatively simple operation requiring only that the desired number of filaments be gathered side by side and given sufficient twist to hold them together.

To produce yarn from short-staple fibers is a much more intricate process mechanically, for just as linear molecules must be oriented to produce a good fiber so, on a macro scale, staple fibers must be parallelized to produce a good yarn. Whatever their source and kind, the tangled mass of staple fibers received at the mill must first be opened out, freed of trash, and worked to a suitable preliminary degree of parallelism and

uniformity by the operation known as *carding*. This operation results in a fluffy, continuous, untwisted strand of uniform density called the *sliver*. A still greater degree of uniformity and parallelism among the fibers is attained by next subjecting the sliver to tension in a number of drawing, or *drafting*, operations. These yield a uniform, continuous, slightly twisted strand known as the *roving*. In making higher grade yarns, short fibers are eliminated from the sliver by *combing*, which is really a continuation and refinement of carding. Combed yarns are cleaner and more uniform in texture with a narrower fiber-length distribution. Finally, the roving is *spun* into a dense finished yarn of the desired weight and strength. During spinning the roving is simultaneously drafted and twisted. Although different staple fibers are all spun in accordance with this one general procedure, the differences in fiber length, diameter, and physical properties require that each be spun on machinery designed particularly for it. Thus there are special machines for cotton, others for wool.

In order to obtain strong, compact yarns it is necessary to impart twist. However, it has been shown that twist is also a source of weakness (Sec. 907) and if carried beyond a certain point reduces strength. For the same degree of twist, long fibers, extending a greater distance within the yarn, give stronger yarns than short fibers.

Twist tends to cause a yarn to kink, which may be undesirable. Furthermore, as twist is increased, a yarn becomes denser, or "harder." Consequently, for the same strength, long fibers yield yarns with less tendency toward kink that are also softer and more supple.

Yarns made from short staple fibers are "fuzzy," owing to the protrusion of fiber ends from the surface. These ends scatter light; as a consequence, such yarns are not likely to possess a lustrous appearance. No such ends protrude from continuous-filament yarns, and the attainment of luster is easier. Cloths woven from them are radically different in appearance from those woven from staple-fiber yarns.

The length *distribution* as well as the average length of staple fibers is important. Very short fibers are a source of weakness and poor quality. It is interesting to note again a striking parallel between the effect of chain-length distribution on a molecular scale (Sec. 904) and fiber-length distribution on a macro scale.

1108. Fiber Cross Section. Natural fibers differ considerably in cross-sectional area and shape as well as in specific gravity (Appendix B). Within limits, artificial and synthetic fibers can be spun to any desired cross section. The *fineness* of a fiber or yarn is its mass per unit length or length per unit mass. One method of stating it is in terms of the *denier* or, more informatively, the *denier count*. The denier is the number of

grams weight in 9,000 m of the fiber or yarn. Much confusion exists because separate branches of the textile industry employ different fineness units. There is a movement afoot to eliminate this by introducing a universal unit, the *grex*, defined as the weight in grams per 10,000 m length. At any rate, it is obvious from these definitions that two fibers may have the same grex or denier and still be of different cross-sectional areas if their specific gravities differ. The term fineness is thus somewhat unfortunate.

By *tenacity* the textile technologist means tensile strength. The tenacity is defined as the breaking strength in grams per denier (or grams per grex). Thus, for a 2-denier fiber whose tenacity is 4 g per denier, the breaking load is 8 g. However, since denier is a function of specific gravity, the tensile strength in the usual engineering units of force per unit cross-sectional area is not proportional to the tenacity and may be calculated only when the specific gravity is known. The following conversion factors may be used:

$$\frac{1 \text{ g/denier}}{0.9 \text{ g/grex}} = \frac{1 \text{ g/denier}}{(\text{sp. gr.} \times 12,800) \text{ psi}} = \frac{1 \text{ g/denier}}{(\text{sp. gr.} \times 9) \text{ kg/sq mm}} = 1 \quad (11-1)$$

Since the denier is a weight, the important thing to note about a fiber tenacity is that it is a strength per unit weight, *i.e.*, a *specific strength* (Sec. 916). The definitions of many other terms relating to textiles will be found in A.S.T.M. Standard D 123.

The simple fact that fibers are very slender beams or columns is a profound determinant of their behavior. It is in this fact that we find the key to the spectacularly different properties of glass en masse and glass that has been drawn into very fine fibers.

The mechanical instability of slender columns has already been discussed in Sec. 915. Fibers buckle so readily that their ability to withstand axial compression is negligible. It is also instructive to consider fibers as cantilever beams.

If a force F is applied to the end of a cantilever beam of length l (Fig. 11-3), the degree of bending is given by the radius of curvature r_c of the neutral axis of the beam. It can be shown that these quantities are related by the expression

$$F = \frac{EI}{r_c l} \quad (11-2)$$

where E is the elastic modulus of the material and I is the moment of inertia of the cross section.

Assuming that the beam (fiber) has a circular cross section, the moment of inertia is such that the above equation becomes

$$F = \frac{\pi d^4 E}{64 r_c l} \quad (11-3)$$

Equation (11-3) shows that, for cylindrical beams made of a given material, the force required to produce a given amount of bending is proportional to the fourth power of the diameter and only the first power of the elastic modulus. Since fibers are beams of extremely small diameter, it follows that even though the elastic modulus of a material may be very

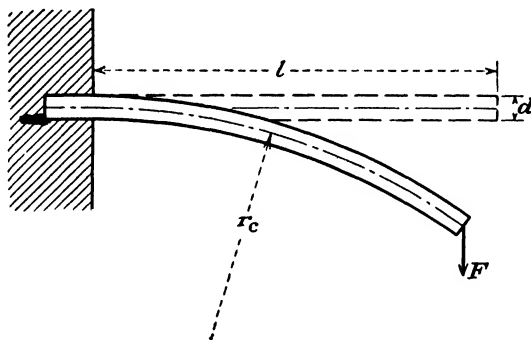


FIG. 11-3. Flexure of a cantilever beam.

high, as for glass, if it is spun into fine enough fibers it will bend readily and hence be supple. To summarize,

1. Doubling the elastic modulus doubles the bending stiffness.
2. Doubling the fiber diameter increases the bending stiffness 16 times.

The denier of a fiber is proportional to the square of the diameter. It follows that the resistance to bending is proportional to the square of the denier, *i.e.*, doubling the denier increases the bending stiffness four times.

Since suppleness, draping characteristics, and other important textile attributes are consequent upon the fiber stiffness, the above facts are of basic importance as guides to manufacturing procedure. It was pointed out in Sec. 906 that, for a given material, fine fibers have higher tensile strengths than coarse fibers. For example, it has been found that very fine cottons have about double the breaking strengths of coarse cottons. It follows that spinning synthetic or artificial fibers to very small diameters will increase both the tensile strength and the suppleness. A yarn of given denier may be attained by twisting together a large number of fine filaments or a small number of coarse filaments. The former procedure is more expensive but yields a better product.

The utility of fibers in general is attributable to their combination of high tensile strength and toughness with suppleness and light weight. The above discussion illustrates how greatly their unique dimensional

attributes contribute to this happy combination. The fields of application for a synthetic fiber are greatly dependent upon how finely it can be spun.

The cross sections of fibers often depart considerably from circularity. This changes the moment of inertia from that used in Eq. (11-3), but this factor is of relatively minor importance and does not seriously affect the discussion.

As usually spun, synthetic fibers are more uniform than natural fibers. For example, nylon fibers show a variation of only 5 per cent, as against about 30 per cent in silk. However, "thick and thin" filament, which varies in diameter, can be made by varying the pressure during spinning. Such filament is sometimes used for yarns to be made into novelty fabrics.

1109. *Spirality, Crimp, and Surface Character.* Ramie, silk, and synthetic or artificial fibers are normally straight tubes or rods. Cotton fibers have a natural spirality. Furthermore, in the wall of the cotton fiber there are alternately spiraling fibrils making a maximum angle of about 57 deg with one another. Wool fibers have a natural crimp, the frequency and amplitude of which vary from one kind to the next. Spirality affects not only the tenacity (Sec. 907) but also the extensibility. Spiraled or crimped fibers possess a certain amount of extensibility that is purely mechanical, akin to that of any other spring. The amount of this extensibility is consequent upon frequency and amplitude.

Since wool fibers are naturally crimped, an ordinary wool yarn is filled with tiny pockets in which entrapped air is held essentially motionless. Woolen blankets and apparel are warm partly because they are wool, but more particularly because of the entrapped "blanket" of quiescent air of low heat conductivity. Imparting artificial crimp to normally straight fibers helps to simulate the properties of wool.

Silk fibers have a smooth surface, while cotton fibers are wrinkled and wools usually have small scales protruding from the surface. As explained in Sec. 1018, luster depends on the ability of a surface to reflect light in a regular, mirror-like fashion. Any roughness or unevenness of the surface breaks up this specular reflection and reduces gloss. The luster of man-made fibers may be varied over wide limits by the techniques mentioned in Sec. 831.

One thing that helps hold fibers together in a coherent yarn is mechanical interfiber friction. A slick, unbroken surface may result in fiber slippage and ultimate weakening of yarn or fraying of cloth. On the other hand, high mechanical interfiber friction such as one finds in wool because of the protruding scales helps to prevent fiber and yarn slippage. Owing to the inherent smoothness of the fibers, rayon fabrics are widely used as linings since garments so lined slip on and off readily. On the

other hand, rayon cloth tends to pull out at seams because of this same smoothness.

1110. Mechanical Properties of Fibers. Owing to their highly anisotropic structure and their characteristic highly elongated form, the mechanical behaviors of fibers are unique. They require special testing procedures and equipment, and besides their applications in textiles and

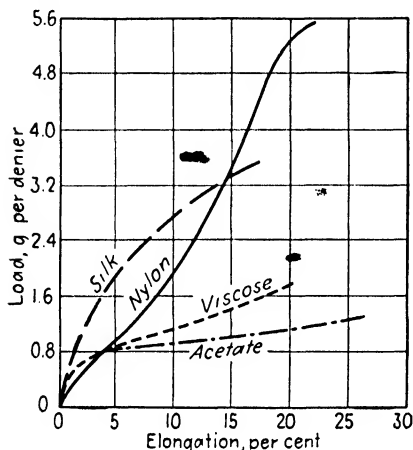


FIG. 11-4. Load-elongation curves of fibers. [G. Loasby, *J. Textile Inst.*, **34**, 45 (1943).]

related products they are widely used as reinforcing materials in molded plastics, rubber, and laminates.

1111. Tenacity and Extensibility. While the physical dimensions of fibers are such that they yield readily to bending or compression, they are strong in tension owing to their polarity and oriented linear-polymeric structure (Appendix B). The tensile strengths are influenced by all the factors discussed in Secs. 902 *ff.*

The elongation at break varies considerably from one kind of fiber to the next. Usually it lies between 1.5 and 25 per cent, but for wool and some specialty fibers it may

be considerably higher. Plasticization by water or other solvents increases the extensibility and may cause either an increase or decrease in breaking strength, for reasons discussed in Sec. 908.

1112. Average Stiffness. Most of the tensile curves available for fibers are load-elongation rather than true stress-strain curves. Load in grams per denier is plotted against elongation in per cent. Humidity, temperature, rate of loading, and other test conditions must be rigorously standardized if reproducible and comparable results are to be obtained. Owing to the plastoelastic nature of fibers and the fact that as tension is applied there is a conversion of unaligned to aligned molecular and crystallite elements, the slope of the stress-strain curve of a fiber is variable, and there is usually no well-defined elastic limit or yield value (Fig. 11-4). There is therefore no definite stiffness or elasticity as defined in Table 7-3, page 265. However, for evaluation and comparison the arbitrarily defined *average stiffness* is very useful. This average stiffness is fundamentally a secant modulus of elasticity between zero load and breaking point and is defined as shown in Fig. 11-5. In this text it will be designated by the symbol E_a . When stated in grams per denier it is a modulus-weight ratio, and it will be seen that it is readily and conven-

iently read off the usual load-elongation diagram. When converted to psi it is the ordinary secant modulus of elasticity. In Appendix B, values are quoted on both bases, and it will be seen that they agree with common experience. Flax is stiffer than cotton, which, in turn, is stiffer than wool.

1113. Toughness. Toughness is one of the most important attributes of a fiber. For comparison purposes, one may use to advantage the simple, readily calculable toughness index W_i , which is defined in accordance with Fig. 11-5. Values are listed in Appendix B on both an equal-weight basis, in gram-centimeters per denier-centimeter, and an equal volume basis, in inch-pounds per cubic inch.

1114. Elasticity and Resilience.

As with all high polymers, when a fiber is subjected to tension, the resulting strain is composed of at least two parts, an instantaneous elastic deformation and a delayed elastic deformation (primary creep). In addition, if the tension is high enough, a completely nonrecoverable deformation due to flow (secondary creep) takes place. If the tension is released, there are an instantaneous elastic recovery (equal to the original instantaneous elastic elongation) and a long-time creep recovery, which, if given sufficient time, equals the original primary creep. The flow deformation (secondary creep), if any, remains as a set (Fig. 7-29, page 300). All this has been dealt with at considerable length in Chap. 7. The important points in connection with fibers are, first, that permanent sets may occur even at low stresses and, second, that the yield points of fibers are usually so indefinite that any definitions of elasticity and resilience must, of necessity, be highly arbitrary and rest on carefully standardized empirical tests. At the current writing such definitions and tests have not been adopted on a wide scale, and truly comparative data are meager.

In regular fiber testing the load is applied at a standard rate of 4 g per denier per min or 12 in. elongation per min. Before the mechanical properties of fibers can be fully evaluated on an engineering basis it is necessary to supplement this test with one at a very rapid rate of loading approaching impact and another at a very low rate approaching relaxation at constant load. One testing machine has been developed that will rupture a fiber or yarn in $\frac{1}{200}$ sec and record stresses and strains by means

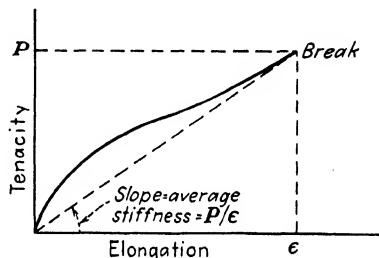


FIG. 11-5. Definitions of fiber properties in terms of tenacity (load)-elongation diagram; average stiffness, $E_a = \frac{P}{\epsilon}$; tough-

ness index, $W_i = \frac{P\epsilon}{2}$. (For definitions of basic mechanical properties of fibers, refer to H. D. Smith, *Proc. Am. Soc. Testing Materials*, **44**, 543 (1944).]

of a wire whose electrical resistance is sensitive to tension and an oscillograph and high-speed camera. The effect of high-speed loading on the stress-strain curve of a nylon is shown in Fig. 9-6b, page 372.

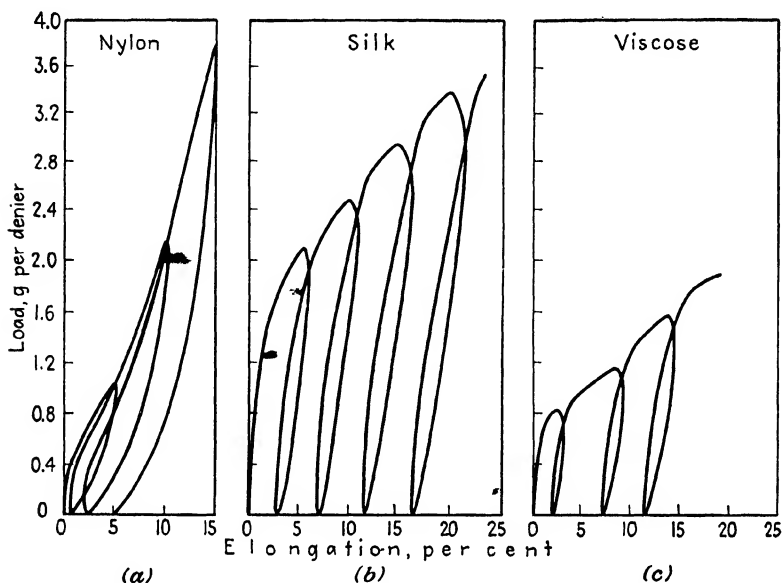


FIG. 11-6. Cyclic load-elongation curves of fibers. [G. Loasby, *J. Textile Inst.*, **34**, 45 (1943).]

Existing constant-rate fiber-testing machines can be used for the measurement of elastic properties by performing a series of loading and unloading cycles. Such a test results in curves similar to those shown in Fig. 11-6. The specimen is stressed to a predetermined strain, *e.g.*, 5 per

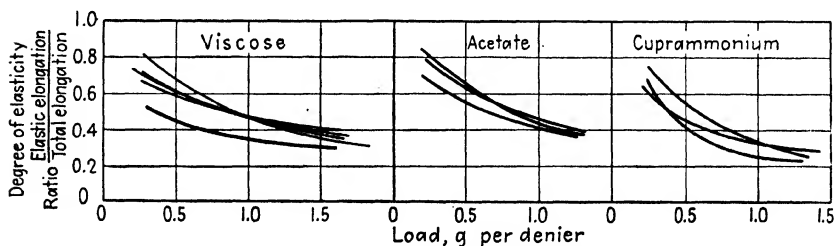


FIG. 11-7. Relation between degree of elasticity and tenacity (load) for some rayon staple fibers. [W. Schramek and F. Hempel, *Monatschr. Textil-Ind.*, **53**, 19 (1938).]

cent, then unloaded to zero stress, then reloaded to a next higher increment of strain, say 10 per cent, then again unloaded to zero stress, and so on, till break occurs. All this goes on at a constant rate of loading and unloading, *e.g.*, 4 g per denier per min, and a series of hysteresis loops is

obtained. (By comparing Fig. 11-6 with Fig. 11-4, it will be seen that the composite of the upper boundaries of the hysteresis loops is a curve very similar to the regular load-elongation curve.) On the basis of this test, it is possible to define the *degree of elasticity* for any given applied stress as the ratio of the strain recovery to the total strain *under these particular test conditions*. For example, from Fig. 11-6a, at a load of 1 g per denier the degree of elasticity is about 85 per cent. With all fibers, as the applied stress is increased, the degree of elasticity decreases. Results on some rayon fibers are presented in Fig. 11-7.

The cyclic test is also used for defining resilience. The *degree of resilience* for any given applied strain is the ratio of the work of retraction to the work of extension. It is the ratio of the area under the unloading curve to the area under the loading curve up to a given strain. In terms of Fig. 7-13, it is the ratio $R/(D + R)$. For any given fiber the degree of resilience changes radically with the amount of strain as shown in Fig. 11-8. So also do the *relative degrees of resilience* of different fibers. For example, for short-time strains of 3 per cent or less, the resilience of silk is equal to or better than that of nylon, while at higher strains nylon's superiority is considerable.

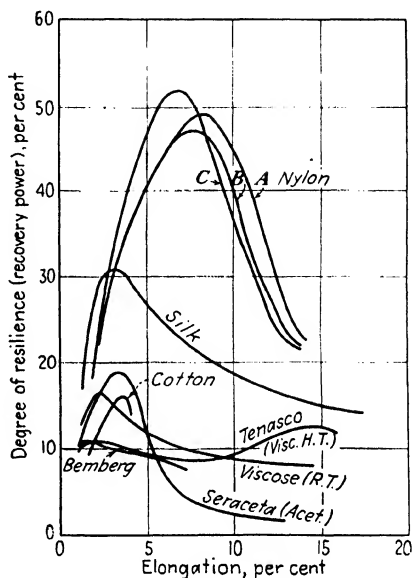


FIG. 11-8. Relation between degree of resilience and elongation for fibers. [G. Loasby, *J. Textile Inst.*, **34**, 45 (1943).]

As previously stated, there is great need for standardization of test methods, the accumulation of a body of comparable test data, and the correlation of such data with performance. Until this is done, little may be said quantitatively about the relative merits of fibers with respect to these properties. Important steps are being taken in this direction.

1115. Discussion. The data of Appendix B show that fibers are generally materials of high tensile strength and toughness with fair to excellent figures of merit (Table 9-9). The range of properties available in different fibers is broad, tenacities and average stiffness varying about a hundredfold and toughnesses about twentyfold. In terms of familiar materials on a comparative basis,

1. Flax is very strong and very stiff but low in toughness and extensibility.

2. Cotton is strong, moderately stiff, moderately tough, moderately extensible.

3. Silk is strong, supple, very tough, extensible.

4. Wool is weak, very supple, moderately tough, highly extensible.

A body of comparable test data on the mechanical properties of fibers must be accumulated and correlated with performance. Consider the following illustration: For most textile purposes, it is desirable to have a material that is both supple and highly resilient. If a standard method of determining a meaningful arbitrary yield point is once established, the comparison and evaluation of fibers will have taken a great forward stride, since the direction of research toward fiber improvement is indicated from fundamental considerations. Thus, using the secant modulus E_y between zero stress and this yield point as the basis of calculation,

$$E_y = \frac{s_y}{\epsilon_y} \quad (11-4)$$

and

$$W_y = \frac{s_y \epsilon_y}{2} \quad (11-5)$$

where s_y , ϵ_y , and E_y are, respectively, the stress, strain, and secant modulus to the yield point and W_y is the resilience (approximate). W_y is the area under the stress-strain curve to the yield point and is equal to $s_y \epsilon_y / 2$ if the curve is assumed to be a straight line, which is only approximately true.

The resilience may be increased in several ways.

1. If E_y can be maintained constant and the yield point increased, s_y and ϵ_y will increase simultaneously and proportionally and the resilience will be increased as the square of either the yield stress or the yield strain with no loss of suppleness.

2. If the yield strain can be maintained constant and the yield stress increased, the resilience will increase directly as the first power of the yield stress but so will the elastic modulus, a loss of suppleness (increased stiffness) being thus entailed.

3. If the yield stress can be maintained constant while the yield strain is increased, the resilience will increase directly with the yield strain but the elastic modulus will decrease and there will be a gain in suppleness.

If method 2 is used for increasing resilience, suppleness may still be maintained in the cloth by spinning finer fibers (Sec. 1108).

1116. The Disalignment Tendency. Alignment along the main axis must be maintained on a macro scale when fibers are spun into yarns. Both fibers and yarns are thus highly anisotropic structures. The oriented molecular and fibrillar arrangement normally represents a state

of low thermodynamic probability and hence low entropy. This is shown by a widespread tendency for these elements to rearrange into disordered masses of higher entropy. Any such disarrangement must of necessity be accompanied by a decrease in length along the fiber axis. For example, when a fiber is immersed in a sufficiently powerful plasticizing liquid, it swells laterally but shrinks axially. If the liquid is subsequently evaporated, the lateral swelling disappears but the axial shrinkage remains. This is demonstrated during the laundering of cotton; the plasticizing action of the heat and polar liquids (soap solutions) may decrease the intermolecular forces of attraction sufficiently to permit

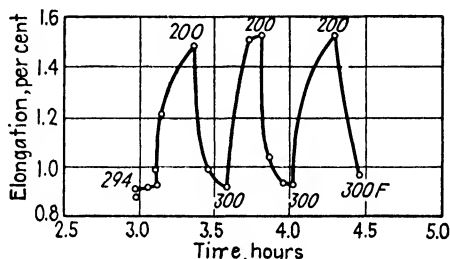


FIG. 11-9. Effect of temperature on elongation of nylon at constant load. [W. F. Busse et al., *J. Applied Phys.*, **13**, 715 (1942).]

the chain molecules to wriggle freely enough to cause considerable disalignment and attendant shrinkage. By contrast, dry cleaning is accomplished with relatively nonpolar organic liquids, and shrinkage is minimized.

After a cord or yarn has been held under a constant tensile load at constant temperature for several hours as, for example, by suspending a suitable weight from it, the creep rate becomes relatively small (Fig. 9-12, curve *B*). If, at this point, the temperature is raised, there is an immediate and reversible decrease in length. The cord returns to (almost) its original length when the temperature is subsequently lowered to its original value. The cycle may be repeated many times (Fig. 11-9). This behavior is the direct opposite of that exhibited by metals and many other nonfibrous masses and was first observed in stretched rubber. It is an interesting demonstration of the Gough-Joule effect (Sec. 1220).

1117. Behavior toward Moisture. A relative humidity of 65 per cent and a temperature of 70 F have been adopted as the standard atmosphere for textile testing and evaluation. The *standard moisture regain* of a fiber or textile is its moisture content when in equilibrium with this standard atmosphere expressed as a percentage of the oven-dry weight (Appendix B).

The amount of moisture absorbed by a fiber and the extent to which

it is plasticized by it depend primarily on chemical constitution but are also influenced by structural features such as the degree of orientation of the molecules. For example, water swells mainly the amorphous regions of a cellulosic fiber, being unable to penetrate the crystallites, and a cotton fiber held under tension swells less than the same fiber relaxed.

Moisture regain increases as the humidity increases (Table 11-2), and

TABLE 11-2. EFFECT OF MOISTURE ON LATERAL SWELLING AND STRENGTH OF SOME FIBER MATERIALS

Fiber material	Moisture regain, %		Swelling in water, % increase in cross-sectional area from air-dry to wet state	Wet breaking strength, % of value at 65 % R.H.
	At 65 % R.H.	At 100 % R.H.		
Wool.....	14.7	33	32	80-90
Viscose, R.T.....	13.1	45	45	45-55
Silk.....	9.5	36	30	75-85
Cotton.....	7.0	25	44	110-120
Acetate, R.T.....	6.0	18	11	65-70
Nylon.....	4.1	8	Slight	85-90
Vinyon.....	0	0	0	100

SMITH, H. D., *Proc. Am. Soc. Testing Materials*, **44**, 543 (1944).

the degree of swelling, tensile strength, elongation at break, toughness, and average stiffness all change as the amount of absorbed moisture changes. In general, relatively nonpolar fibers and those in which the molecules are most highly oriented are least affected. Average stiffness universally decreases and elongation at break increases as the amount of absorbed moisture increases, but no such uniform trend is shown in toughness or tensile strength. For some fibers these latter properties increase, while for others they decrease with the weight of moisture absorbed. Possible reasons for this phenomenon were advanced in Sec. 908.

The magnitude of the difference between the dry and wet strengths may be taken as a general index to the moisture sensitivity of a fiber and its tendencies to shrink, stretch, or sag in a changing humidity environment.

YARNS

1118. Although yarn properties are derived from the character of the fibers from which the yarn is spun, they are considerably modified by form factors superimposed by the structure of the yarn itself, as shown by the following examples:

As previously stated, fibers must be given twist to produce yarn.

If hard, dense yarns are desired, the twist must be extensive. If soft, full yarns are needed, the amount of twist will be small, often at a sacrifice of strength. Only a fraction of the total fibers in a cross section of staple-fiber yarn breaks at rupture. Even in a well-made cotton yarn, no more than 70 per cent break; the others "pull out." Sometimes two or more yarns are twisted together; this is a *ply*, or *folded*, *yarn*. Just as thin fibers have higher tensile strengths than coarse fibers, so a ply yarn is stronger than a single yarn of the same weight. For these reasons there is no quantitative correlation between single-fiber strength and the strength of yarn made from that fiber. Anywhere from one-half to two-thirds of the potential fiber strength is ordinarily sacrificed in converting fiber to yarn.

The part played by the purely mechanical factors introduced when fibers are built up into yarns is further illustrated by the behavior toward moisture; a cotton yarn gains considerable strength between 50 and 100 per cent relative humidity, a region in which cotton single-fiber strengths remain practically constant (Table 9-8, page 370).

Novel style effects and great variety in fabrics are the lifeblood of the clothing industry. Unique effects may be produced by making ply yarns out of singles with different degrees of twist, as well as by merely varying the over-all amount of twist. Diversity may also be attained by spinning "blended" yarns from a mixture of different fibers—cotton and wool, silk and rayon, cotton and rayon, nylon and glass, silk and wool, etc.

The first man-made fibers to attain commercial stature were the rayons. In the early days of the industry, practically all rayon was produced as continuous-filament yarn. Among the contributory reasons were the following:

1. Continuous filament yarns are easier to make than staple-fiber yarns and with less sacrifice of strength.
2. The early rayon manufacturers were obsessed with the desire always to simulate the luster of silk.
3. Methods for successfully and evenly dyeing mixtures of natural and artificial fibers had not been developed.
4. Properties of the early rayons were not good enough to stimulate enthusiasm over mixed yarns of natural and artificial fibers.

As time went on the properties of the rayons were improved, and successful dyeing techniques for blended yarns were developed. Through control over the process, it is possible to produce artificial *staple* fibers of almost any required length, diameter, denier, or luster. Artificial staple fibers are made by gathering a large number of continuous filaments into a tow and chopping them to the desired length. The entire range of staple lengths and denier counts encountered in natural fibers is easily

covered, and thus it is possible to produce to order rayon staple fibers that can be successfully spun for almost any machine, either per se or blended. The range of fabric properties and styles is greatly broadened. The production of staple fiber rayons expanded steadily until in 1940 and subsequently it exceeded continuous filament production. Most other man-made fibers are also being produced in staple lengths.

FABRICS

1119. As previously stated, fabrics are made by three fundamental techniques—weaving, knitting, and felting. Within each category there are many different modifications. The important point is that not only may yarns of different appearance and character be made from one kind of fiber but also the range of properties may be still further broadened by variations in the mechanical techniques of making fabrics. The ultimate result is a very striking spread in appearance, properties, and applications. Thus, a serge suit, a tweed suit, a sweater, and a felt hat may all be made from wool. Furthermore, when yarns are built up into a fabric, a new set of mechanical forces is introduced. The behavior of a fabric is therefore a complex composite of which fiber behavior is just one factor.

1120. Hand. In industrial fabrics like filter cloth or belting, appearance and “feel” are minor factors overshadowed by strength and resistance to solvents, chemicals, etc. However, in apparel and furniture fabrics the reactions produced on the senses, particularly those of sight and touch, often come before all other considerations.

Hand is the term used to describe the complex reaction produced on the human senses when a fabric is examined visually and tactually. Hand embraces such factors as whether the fabric is springy or limp, “warm” or “cold,” pliable or stiff, rough or smooth, thick or sheer, and how it falls into drapes or folds. Working from the molecular structure up, these qualities depend upon the structure and chemical composition of the fibers, the fineness, twist, and fuzziness of the warp and filling yarns, the nature, regularity, and closeness of the weave of the fabric, and the nature of the sizings, dyes, softeners, waterproofings, and other coating and finishing agents with which the fabric may have been treated.

Good hand is not always synonymous with good quality. By clever use of sizings, etc., inferior fabrics may be dressed up to give deceptively good original hand, which, sadly enough, disappears rapidly during service.

1121. Drying Characteristics. Moisture regain is an index to how rapidly a fabric will dry after washing, a prime consideration in some fabrics such as those for women’s stockings. Thus viscose stockings must

be allowed to dry 36 hr or more after rinse laundering if they are to be worn without danger of tearing or pulling out of shape; silk stockings dry overnight; nylons may be worn after only a few hours (Table 11-2).

1122. Shrinkage. During ordinary washing a fabric is subjected to the powerful plasticizing action of a warm or hot electrolyte solution (soap and alkali). Unless proper measures are taken, sufficient permanent shrinkage may result to ruin the material or garment. Laundry shrinkage may be as much as 40 per cent for wool and 20 per cent for cotton fabrics. As little as 2 per cent may render a shirt uncomfortable or even unwearable.

Laundry shrinkage may arise from three causes, as follows:

1. The shrinkage occurring in a single fiber is the result of molecular or fibrillar disarrangement or rearrangement, as previously discussed. If laundering conditions are such that they can cause single fiber shrinkage, naturally the whole fabric will shrink.

2. Shrinkage can also result if there is a strong tendency for fibers and yarns to felt with one another.

3. Finally, in the ordinary spinning, weaving, and finishing of yarns and fabrics the material is held under tension and the finished goods are left in a strained condition. Unless these strains are eliminated beforehand, they will be relieved during the first laundering and will constitute the major cause of shrinkage in all fabrics, with the possible exception of wool.

Shrinkage from the first two causes is more or less inherent but luckily is of minor extent except in wool, which is the problem child of fibers in this regard owing to its unusual structure (Sec. 529). But there is no legitimate excuse for not eliminating shrinkage attributable to the third cause before a fabric reaches the consumer. Various methods may be employed. In connection with cotton and other cellulosic goods, many attempts have been made in the past to overcome this type of shrinkage by (1) treating the cloth chemically, (2) wetting the cloth and then drying it under as little tension as possible, or (3) actually washing the fabric. The first two of these methods do not result in complete shrinkage. The third method, while producing a completely preshrunk cloth, is cumbersome and expensive and destroys the "new-goods" appearance. A far more effective device is the process known as *Sanforizing*. The maximum amount of shrinkage that the fabric will undergo during laundering is determined by actual test of samples. The cloth is then run through an ingenious machine that imparts a definite and controllable mechanical crimp along both the warp and the filling. The underlying principle of the machine is that the cloth is shortened by being dried while under linear compression. When the fabric is subsequently washed, true shrinkage

occurs but this is compensated by an accompanying loss of the mechanical crimp in both the warp and filling yarns so that the net change in dimension is practically zero. Textile manufacturers cannot, however, treat cloth in a manner to render it impervious to the damage accompanying patently overdrastic laundering.

One method of producing crepe is to weave a fabric from yarns that shrink to different extents.

The prevention of shrinkage in woolen fabrics requires different techniques (Sec. 1133).

1123. Ironing and Boarding. When a fabric is ironed, many of the fundamental techniques of plastics molding are utilized. Thus, to remove wrinkles and put a preferred crease into a pair of trousers, the fabric is moistened (temporary external plasticizer), and heat and pressure are applied by means of the iron until the fabric has been "molded" to the desired shape. Much the same techniques are involved in hat blocking. On a damp day, when the amount of external plasticizer in the air is high, a crease is soon lost. Each fabric requires its own ironing temperature, which must be high enough to be effective but not so high as to cause damage. Under too hot an iron, nonthermoplastic fibers will scorch, while thermoplastic fibers will actually fuse. As each new man-made fiber is introduced on the market, a program of consumer education is required with regard to proper ironing and laundering procedures for the fabrics woven from it.

Certain items, notably women's stockings, must be carefully shaped before reaching the consumer. This is accomplished by the operation known as *boarding*. Each stocking is drawn over a special leg-shaped metal or wood form, subjected to a treatment with steam, and then permitted to dry. For nylon hose the treatment is 5 min with steam at 5 lb gauge pressure (228 F). The water and heat act as temporary plasticizers. During this treatment the fabric takes a set and thereafter tends to stay true to dimension and shape unless subsequently subjected to still more drastic conditions, which is unlikely in the normal course of events. Ordinarily, thermoplastic fibers exhibit too much creep or cold flow to be used for stockings or other garment fabrics subjected to stress over long periods of time. They would develop permanent bags at the knees or otherwise lose shape. Nylon, however, is a thermoplast of exceptional strength and resilience and is able to compete successfully with silk.

1124. Warmth. If two fabrics at the same room temperature are handled, one may feel warm, the other cold. The sensory response depends, not merely on temperature gradient, but also on rate of heat transfer. Among the factors involved in this complicated phenomenon

are the thermal conductivity and specific heat of the fibers comprising the fabric, the number of air spaces in the fabric, and the rate of evaporation and transfer of moisture from the skin to the fabric, which, in turn, depends upon the construction and porosity of the fabric as well as the water-absorptive character of the fibers comprising the fabric. Visual response plays a subtle part in that red fabrics are inclined to "feel" warm, blues cold.

The thermal conductivity of the single fibers, although a contributing factor, does not play a dominant role in determining the actual insulative value of a cloth. Much more important are the thickness, weave, number and size of air spaces between fibers, and rate of moisture absorption and transpiration. For example, tests show that the thermal conductivity of camel's-hair fibers is 50 to 65 per cent that of wool fibers. However, on an equal-weight basis, camel's-hair cloth is only 6 to 35 per cent a better thermal insulator than wool cloth, depending on weave and construction.

A garment that is to be worn next to the skin must be made of fabric that can "breathe." Otherwise, perspiration cannot escape and discomfort to the wearer results. Knit underwear, being more porous, is better than woven. Tightly felted material would be entirely unsuitable.

FELTS

1125. The fundamental problem involved in making a felt is to cause fibers to intermesh and adhere in a dense, continuous mat. Both the molecular and gross structure of the fibers are important determinants of the felting properties.

1126. Paper. If cellulosic fibers obtained from wood pulp or rags are suspended in a liquid and the liquid is then drained off through a screen, a layer of randomly disposed intermeshed fibers is left behind. When this is dried and subjected to pressure between rolls, the resulting sheet is practically devoid of mechanical strength and does not constitute a strong paper. Evidently something other than mere mechanical entanglement is necessary to make the fibers bond into a strong felt.

1127. Papermaking in Outline. Papermaking may be outlined briefly as follows:

1. A cellulosic material, whatever its source, receives a preliminary treatment to remove dirt and other objectionable matter.

2. The cleaned stock is then reduced to a pulp of individual fibers by mechanical or chemical methods or both.

3. The resulting pulp is then suspended in water in a beating machine called a *Hollander*. Here, for considerable lengths of time, it is subjected simultaneously to the swelling action of the water and mechanical

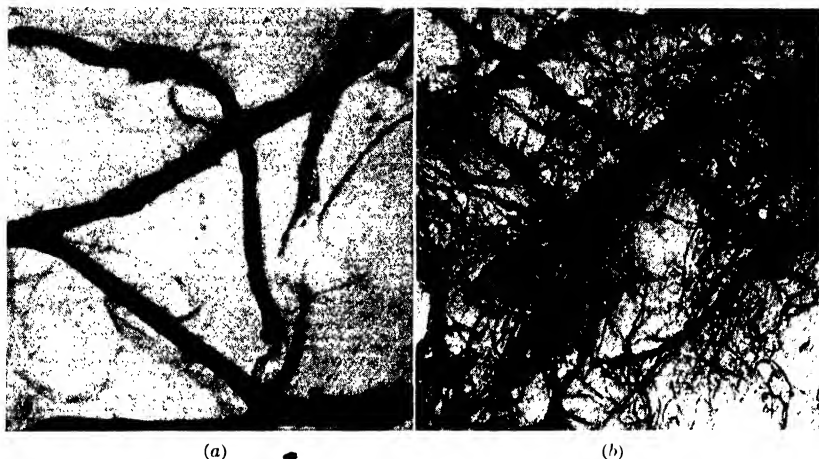


FIG. 11-10. Fibrillation of fibers produced by beating cotton rag stock ($\times 100$). (a) Unbeaten. (b) Cotton rag stock, beaten. (Courtesy Institute of Paper Chemistry.)



FIG. 11-11. Electron microphotograph ($\times 30,000$) of a mechanically opened cotton linters fiber. [Hercules Chemist, No. 16 (June 1946).]

rubbing, maceration, and mauling, during which each fiber splits, frays, and opens out into a great number of slender fibrils (Figs. 11-10 and 11-11). Furthermore, the fibers become highly swollen and take on a somewhat gelatinous character. The beaten stock has a slippery, shiny feel, and

it is difficult to squeeze the water out of a handful of it. This change is called *hydration*. The beating process is the crucial step in papermaking as evidenced by the fact that unbeaten stock does not form strong paper, while beaten stock does. Fillers and sizes may also be introduced in the Hollander to impart special properties to the finished paper.

4. The beaten pulp in the form of a dilute (0.5 per cent) suspension flows continuously onto the fine-mesh wire screen of a so-called "Four-drinier machine." This screen moves forward, at the same time being given a vibratory, sidewise motion to induce the hydrated, frazzled fibers to intermesh into a weak but continuous web. While the mass is on the screen, the free water is drained from it, the process being aided by suction.

5. The wire screen carrying the paper web finally reaches a perforated cylinder known as the *couch roll*. At this point the paper web is automatically lifted off the wire screen and transferred to an endless belt made of wool felt.

6. The web is next squeezed between a series of press rolls, which force out more water and densify the web.

7. At the end of this pass the sheet possesses sufficient mechanical strength to be sent over a series of steamheated drying cylinders, and during this process bound water is removed by evaporation. The sheet shrinks throughout this process. Hence the speeds of the drying cylinders must be perfectly synchronized, or the sheet will break.

8. The dried paper then passes between calender rolls, which give it a hard, dense surface. If a highly polished surface is desired, it is passed between differential rolls.

1128. *The Effects of Beating and Hydration.* It is essential to consider carefully the following facts and conclusions concerning beating in a Hollander:

1. Fibrillation and hydration do not take place to any noticeable degree unless the beating is conducted in a strongly polar liquid capable of acting as a swelling agent (Table 11-3).

2. When water, a polar liquid, is used, the primary wall (Sec. 525) is cracked, torn, and at least partly removed and a splitting or unraveling into fibrils visible at relatively low magnification takes place.

3. Appreciable swelling occurs. However, this swelling does not noticeably increase with beating until the fiber structure has been loosened by the plasticizing action of the water.

4. An exceedingly fine fibrillation of fuzz takes place on the surface of the secondary-wall material. This fuzz is very difficult to detect with an ordinary microscope but is readily observed with an electron microscope.

5. The average fiber length is reduced, since wet fibers are not strong and are rather readily cut by the bars of the beater.

6. There is a rapid increase in specific surface, *i.e.*, exposed area per unit weight of cellulose, especially during the initial stages of beating. Beaten stock hydrolyzes faster than unbeaten stock.

7. No change in x-ray pattern accompanies beating. Therefore the "hydration" is a nonpermutoid reaction; both beaten and unbeaten fibers exhibit the native crystalline form (Sec. 527). Undoubtedly, the water taken up during hydration forms hydrogen bridges with the alcohol groups of the cellulose, but only in amorphous regions and on crystallite surfaces.

8. No change in chemical composition of the cellulose takes place.

9. There is a minor decrease in the average degree of polymerization; the copper number increases slightly, the alpha-cellulose content remains unchanged, while the cuprammonium solution viscosity decreases slightly.

10. As the plasticized fibrillated beaten mass is caused to mat together on the screen of the Fourdrinier machine, there is far greater interfiber contact area than exists among matted unbeaten fibers. As the water is removed by evaporation, the mat shrinks and hydrogen bridges between the fibrils are re-formed; but now the bridging ties the fibrils together in the form of a tightly felted sheet of paper. Since the number of these newly formed bridges and the degree of mechanical interlocking are both much greater among beaten fibers than among unbeaten, the felt resulting from the former is denser and stronger than that from the latter.

11. (a) Paper made from unbeaten or slightly beaten stock is opaque, soft, mechanically weak, and absorbent, manifesting little or no resistance to penetration by liquids; a good example is blotting paper. (b) Paper made from very well-beaten stock is translucent, denser, and stronger and somewhat resistant to penetration by oil; an example is imitation parchment. (c) Still further beating plus heavy calendering yield a transparent, hard, dense paper with considerable resistance to oil, *e.g.*, glassine paper. If a sheet of dry glassine paper is heated, it blisters because of the formation of bubbles of steam within the sheet. Glassine paper coated with paraffin wax is resistant to penetration by both moisture and oil and is a good wrapping for foodstuffs.

12. Long-fiber pulp stocks make stronger papers than short-fiber stocks; rag bond papers are an illustration.

13. The tensile strength of the finished paper increases with beating time but plateaus off at longer beating times. Tearing strength rises during the early stages of beating but then diminishes progressively. The ability to withstand repeated folding (folding endurance) also rises to a maximum and then falls rapidly. Excessive beating reduces the

bursting strength of the final paper. These effects, shown in Table 11-3, are explained as follows: Beating causes fibrillation and hydration, which lead to increased paper strength; but it also tears and reduces the average fiber length, which has the opposite effect of reducing the strength. The paper strengths, therefore, pass through optimum values.

TABLE 11-3. EFFECTS OF LIQUID POLARITY AND BEATING TIME ON PROPERTIES OF FINAL PAPER

Beating liquid			Beating time, min	Properties of final paper		
Name	Dielectric constant	Swelling action on cellulose, % increase in volume		Bursting strength	Folding endurance	Oil-penetration time, min
Water.....	80	90	Unbeaten	85	2,970	0
			80	101	1,310	4
			160	109	900	21
			240	135	40	120
			Unbeaten	14	2	0
Butyl alcohol.....	18	4	80	10	0	0
			160	8	0	0
			240	8	0	0
Fuel oil.....	2	2	480	0	0	0

1129. Other Paper Processing. Many different kinds of paper are produced by the use of various fillers, sizes, coating materials, colors, and other compounding ingredients. By treating paper with powerful permutoid-type swelling agents, strong bonding between sheets may be obtained. For example, rag or sulfite paper is saturated with a 75 per cent solution of zinc chloride at 40 C and then wound on a mandrel and allowed to coalesce. It is next washed, dried, and pressed or calendered to form an exceptionally dense, tough, strong product called *vulcanized fibre* suitable for electrical and heavy-duty applications. *Parchment paper* such as that used for wrapping butter is made by treating paper sheets with cold concentrated sulfuric acid for about 15 sec, then washing free of acid, and finishing. The process makes the paper somewhat translucent and imparts a high wet strength.

1130. Wool Felts. One of the most notable characteristics of wool fiber is the outstanding ease with which it forms strong felts. Felting makes possible the production of very dense, strong fabrics suitable for

hatmaking, etc. It also facilitates the production of remarkably strong cloths from short-fibered wools. These cloths would otherwise be weak.

1131. The Wool-felting Operation. In the operation variously known as *felting*, *fulling*, or *milling* a loose web of wool fibers is subjected to repeated impact by a mechanical arm while immersed in a warm solution of an electrolyte at a suitable pH. Under this treatment the fibers shrink and interlock into a fabric of greater strength and density. The process may be applied either to woven material or to masses of unspun fibers. Depending on the amount of felting desired, the mechanical impact may be more or less drastic, and the time of milling may vary from a few hours to as long as several days.

To the extent that the fibers are exposed to the simultaneous action of a polar swelling agent and mechanical treatment, the felting of wool resembles the beating of paper pulp, but there are important differences. Mechanical action is necessary, but it must not be so vigorous as to break, fibrillate, or otherwise damage the fibers. As with pulp beating, wool felting does not occur to any great degree in nonpolar liquids. Experience has shown that optimum results are obtained with temperatures around 45 C. Aqueous solutions of either high or low pH are effective; but although felting takes place rapidly in acid solutions, it is usually performed in soap and soda solutions at a pH around 10 since this leads to greater softness and better hand in the finished product.

1132. Mechanisms of Wool Felting. So many factors can and probably do contribute to the felting of wool that this phenomenon is a very complicated one.

In most fine wools the edges of the scales are smooth and straight, whereas in coarser wools the edges are often serrated. In some wools, the scales lie flat and tilelike. Such wools have a hairlike texture. They are generally stiffer and straighter and do not so readily form felts. By contrast, the epidermal scales of other wools project toothlike from the cortical shaft for about one-third their length. Such wools are likely to show particularly marked felting tendencies. The scales act as ratchets, restricting the motion of one fiber past others to one direction. Their mechanical interlocking during milling is undoubtedly one factor contributing toward felting. That it is not the only one is shown by the fact that certain wools with strongly serrated scales are not of good felting quality.

In passing from one sample of fibers to another there is a well-defined relation between fineness and natural crimp. Fine wool fibers are generally soft and wavy. Coarse wools show little or no waviness. It is a matter of experience that waviness and good felting properties show a correlation, but whether the enhanced felting properties are due to the waviness, fineness, softness, or all three is not clear.

Besides the above-described effects depending only on features of the gross structure of the fibers, other factors are unquestionably involved. During felting the combined plasticizing action of the electrolyte solution and heat is great and prolonged; and as pointed out in Sec. 529 drastic plasticization may lead to supercontracted wool with a fiber length only two-thirds that of the original. Such supercontraction obviously means shrinkage and densification. Furthermore, the plasticizing and solvating of fiber surfaces may eventually cause them to coalesce to form a more or less continuous structure, new *interfiber* salt bridges forming when the felting liquid is removed from the densified mass. At any rate, microscopic examination of a tightly felted wool gives the impression that the fibers are "glued" together rather than merely intermeshed mechanically.

1133. Laundry Shrinkage of Wool Fabrics. The same shrinking and felting properties so valuable in the manufacture of wool felts often prove to be a curse in the laundering of woolen garments. A piece of wool fabric may shrink as much as 45 per cent, becoming "boardy" in the process and, of course, unwearable as to size.

Spinning, weaving, and knitting leave the usual internal stresses in woolen textiles, and shrinkage will result the first time the fabric gets damp or wet. These stresses must be released before the fabric is marketed. In woolen goods this is accomplished by the operation known as *crabbing*, which is a short treatment of the fabric with steam or boiling water while under slight tension. In spite of this, laundry shrinkage tends to take place because of felting, which occurs to a limited extent even during proper laundering. Careless laundering in media whose plasticizing action is too great (solutions too hot or too strongly alkaline) causes so much supercontraction and shrinkage that a garment may be rendered unusable. Dry cleaning, which is a low-temperature treatment with nonpolar liquids, is much safer.

Many attempts have been made to produce unshrinkable wool by treatments with chlorine gas, hypochlorite solutions, solutions of caustic in alcohol, and solutions of sulfuryl chloride in white spirit. All these reagents depend for success on the rupture of the cystine links of the wool keratin (Sec. 447), especially in the epithelial scales and the layer of cortex immediately underlying the scales. None of these methods may be considered commercially successful because they only partly eliminate shrinkage, impair the hand or appearance, or seriously reduce the strength and wearing properties.

A different approach is to reduce the felting power by modifying the elastic properties of the fiber by the technique of polymerizing resins *in situ* throughout the fiber. This method is described below in Sec. 1142 and is so effective that it may be said that "unshrinkable wool" is now practically an accomplished fact.

1134. Dry Felting. The wet process previously described for the felting of wool depends for its success on properties unique to wool fibers. Until the discovery of synthetic thermoplastic fibers, wool and similar animal hairs were the only materials that could be satisfactorily felted.

If polyvinyl chloride-acetate staple fibers in correct amounts are intermixed evenly with other fibers and the resulting mass is heated and pressed, the thermoplastic polyvinyl chloride-acetate filaments fuse together at all points of contact, forming a continuous reticulated framework that binds the entire mass into a satisfactory felt. By this simple dry-felting process it is possible to make felts of almost any fibrous material, including asbestos, glass, and all sorts of fiber mixtures with highly desirable properties for industrial, household, and clothing applications. Strong reinforcing cloth laminations may be sandwiched between two felt layers and the assembly then hot-pressed. Binding fibers other than polyvinyl chloride-acetate may be employed. The fundamental requirement is merely true thermoplasticity.

1135. Leather. Animal skin or hide is a natural felt of intermeshed protein fibers. It is converted to leather by tanning. Since its structure en masse as it comes from the animal is a predetermined fact, the tanner cannot modify the texture and hand of leather to the same extent as a textile manufacturer can those of cloth. Nevertheless, it is possible to produce essentially two kinds of products, "light" leather, which is soft, flexible and porous, *e.g.*, that used for gloves and shoe uppers; and "heavy" leather, which is stiff, nonporous, and abrasion-resistant, *e.g.*, that used for shoe soles and luggage. For the first, chrome treatment is more suitable since this tanning process is a sort of vulcanization involving the introduction of relatively small amounts of material into the pores of the structure. For the second, vegetable tanning is better suited since it consists fundamentally in the introduction of large masses of reinforcing filler into the pores of the felt. Patent leathers are leathers with a high gloss surface coating.

1136. Properties of Animal Skins. A skin is composed of a thin outer *epidermis*, about 1 per cent of the total thickness, and thick inner *derma*, which is essentially a porous mat of intermeshed, disordered protein fibers. Bonding tissue is also present. Hair follicles, sweat glands, oil glands, nerves, fat cells, and blood vessels are other integral features of the structure. That part of the derma next to the epidermis is particularly dense and chemically resistant and leads to the highly desired grain surface of some finished leathers.

The epidermis is mainly keratin, which is particularly susceptible to attack by alkali and sulfides (Sec. 447). By contrast, the fibers of the derma consist mainly of the protein collagen, which is more susceptible

to hydrolysis by acids than bases. It is therefore possible by suitable treatment with bases to remove the epidermis while leaving the derma comparatively unattacked. Hot water very slowly hydrolyzes collagen to gelatin, which goes into solution; but it does not attack elastin, the protein of the bonding tissue. On the other hand, the enzyme trypsin preferentially attacks elastin, causing it to dissolve. Trypsin also catalyzes the hydrolysis of gelatin. The varying chemical behaviors of the several protein components and layers of the hide are of basic importance since in the manufacture of leather it is essential to remove the epidermis, elastin tissue, etc., and leave the collagen fibers of the derma available for further treatment.

Collagen, like wool keratin, is chemically complex, consisting of at least 18 different kinds of amino acid units (Table 4-10). The chain molecules of the collagen fibers of skins and tendons are normally in an extended condition like those of silk. There is an x-ray fiber pattern; but, owing to the low main-chain symmetry traceable to the many proline and hydroxyproline units, crystallinity is of a low order, and the pattern is not sharp. In a tendon, the collagen fibers are aligned. When it is warmed, it undergoes a large shrinkage to one-third its original length owing to thermally induced coiling and folding of the chain molecules. The shrunken, denatured mass is somewhat rubbery.

Untanned hide has serious shortcomings. It is highly susceptible to putrefaction. It is only fairly strong and too readily stretches out of shape under stress. Although essentially insoluble, it is extremely sensitive to water. Under the plasticizing influence of moisture it swells extensively into a soft, stretchy mass. On drying, the plasticized skin contracts and becomes cemented into a hornlike, boardy mass, which cracks easily. In hot water it shrinks greatly for the reason already mentioned. Furthermore, the shrinkage temperature is low, in the neighborhood of 55 C.¹

Put briefly, untanned hide is too highly plastic. Any treatment that will eliminate or minimize these shortcomings is called tanning, and the improved product is what we know as leather. Tanning may be accomplished by a variety of agents. Usually the skin is exposed to the action of an aqueous dispersion of the tanning agent in a long, deliberate process requiring weeks or months.

1137. Preparation of Hides. Since animal skins are protein, which is amphoteric, pH control is highly essential in the processes and operations of leather manufacture. Swelling is least in the isoelectric zone (for

¹ When leather or hide is gradually heated in an aqueous medium, a temperature is encountered at which noticeable shrinkage starts. This is defined as the *shrinkage temperature*, an important quantity that can be used to judge the extent of tanning.

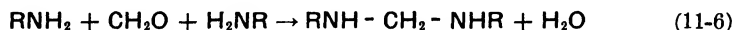
lime unhaired hide, pH 4.8); basic groups are more active on the acid side and acid groups more active on the alkaline side of the isoelectric zone (Sec. 446). Before hides can be tanned they must undergo several steps of preparation, which take place in the *beamhouse*. The skins are washed and soaked to remove dirt and blood and to plump them up. Trimmings are cut away by hand, and adhering flesh is removed by the knives of a fleshing machine.

The hair and epidermis are removed, most usually by soaking in a dilute milk of lime, often with added sodium sulfide. At the pH and temperature used, hydrolytic attack occurs preferentially in the keratin of the hair and epidermis [Eq. (4-52), page 152], the collagen and elastin being but little affected. The process is called *unhairing*.

To obtain a clearer grain surface or softer leather the unhaired skins are washed and then bated. *Bating* is a treatment with a solution of pancreatic enzymes usually buffered with ammonium chloride. Elastin and gelatin are attacked and removed, but the collagen fibers of the derma are practically unaffected. This removal of part of the protein leaves the skin softer and more porous. Not all skins are bated.

After unhairing and bating, the skins are washed to remove alkali, etc. Most usually, they are pickled with a liquor containing acid and salt and are then ready for tanning. The amount of acid and salt added controls the extent of swelling (plumping) in accordance with the Donnan equilibrium.

1138. Tanning with Formaldehyde. When a prepared skin is treated with a solution of formaldehyde, the latter reacts with the collagen and the following changes take place: The treated product swells much less in water. The shrinkage temperature is raised considerably, to the neighborhood of 80 C. The tensile strength increases. Although the formaldehyde-treated product contracts on heating and shows somewhat rubbery elasticity, it undergoes much less plastic deformation than the original hide. In short, the skin has been tanned. These changes will be recognized as typical of those accompanying mild cross-linkage. Indeed, the properties of the skin resemble those of mildly vulcanized rubber. Only about 0.5 per cent of combined formaldehyde is required to effect these extensive changes. The probable mechanism for this type of tanning is the introduction of primary-valence cross-links between the collagen fibers in accordance with



Formaldehyde tanning is irreversible. The cross-links cannot be broken without disrupting the collagen molecules.

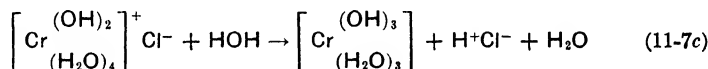
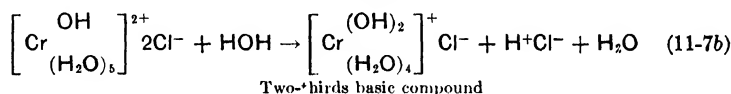
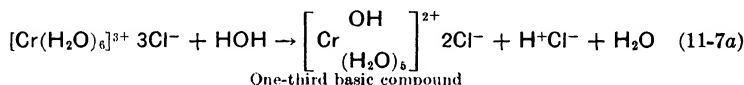
Although many materials including formaldehyde act as tanning

agents, by far the most widely used at the current writing are basic chrome salts and vegetable tannins, which serve to divide leather goods into two major categories, chrome-tanned and vegetable-tanned.

1139. Chrome Tanning. Chrome tanning is usually conducted by treating prepared hide on the acid side of the isoelectric point with basic chrome salts. Insoluble basic chrome compounds are deposited in the hide during this treatment.

Because this type of tanning involves the fixation of complex cations into the skin, it is termed *cationic tanning*.

When cationic coordination chrome salts that contain complexly held aquo groups are hydrolyzed, a basic chrome salt (containing OH groups) is formed, together with free acid.

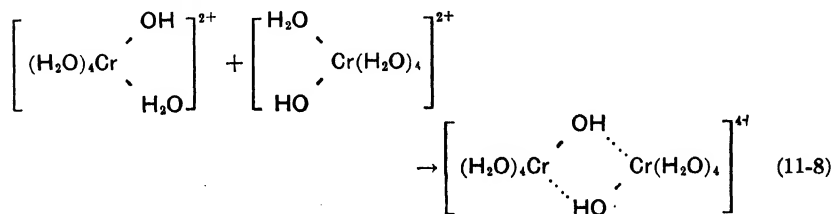


These hydrolyses are accelerated by the addition of alkali.

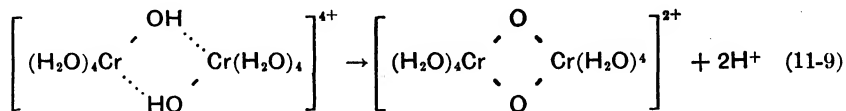
Generally speaking, only those chrome compounds which are basic or can become so in solution have tanning power. For most chrome tanning the one-third basic compound is used, usually in the form of sulfate.

On introduction of skin substance, its basic groups combine with free acid of the solution until the acid-combining capacity of the protein has been used up. During this process chrome compounds are deposited in the skin.

Basic chrome complexes undergo olation, leading to an increase in molecular weight and decrease in solubility. Hydroxy groups are held by two chromium atoms, one via primary bonding, the other by secondary valence bridging.



Olation is favored by time, heat, increased basicity, and increased concentration. Further hydrolysis can lead to further olation, with the formation of longer chain complexes. Oxolated complexes may form with the liberation of acid.



Heat and time favor this last reaction. The oxo complexes are more stable and more acid-resistant than olated compounds.

Several important facts have currently been established about chrome sulfate tanning.

1. There is a quantitative interdependence between the fixation of acid by the skin and the amount of chrome deposited.
2. When the acid-combining capacity of collagen is used up, it has no further ability to fix chrome.
3. Regardless of the original basicity of the chrome used, the chrome first deposited in the hide is the two-thirds basic compound. After deposition the two-thirds basic chrome compound very probably undergoes further hydrolysis and olation.

There are two approaches to the interdependence of acid fixation and chrome fixation in cationic tanning. One is that the fixation of acid by the basic protein groups results in deposition of the insoluble chrome without necessarily involving the acidic groups of the protein; *e.g.*, amino groups of the protein remove acid from the liquor, promoting hydrolysis in accordance with Eq. (11-7*b*), which leads to the formation and deposition of highly basic chrome. The other hypothesis is that the cationic chrome is fixed by acidic groups of the protein while the hydrolyzed acid of the liquor is simultaneously fixed by the protein basic groups. Either view accounts for the interdependence of acid fixation by the protein and chrome deposition.

Since it is well known that chromium forms very stable coordination compounds containing both carboxyl and amino groups as in oxalato and ethylenediamino complexes, it is natural to postulate that in chrome-tanned leather an olated or oxolated chrome could serve to bind together collagen chains or fibers by coordinating with their carboxyl and amino groups. The resulting structure would be cross-linked and hydrophilic groups would be blocked off. This would account for the increased tensile strength, shrinkage temperature, and resistance to putrefaction and the decreased swelling in water. The facts that as little as 2.5 per cent of fixed chromium based on the weight of the hide is capable of giving a satisfactorily tanned product and that chrome tanning may raise the

shrinkage temperature to very high values ($> 100^{\circ}\text{C}$) lend substance to such a vulcanizing mechanism rather than mere mechanical blocking or filler action. Under the microscope a chrome-tanned skin looks "empty." Interfiber voids are prominent. This explains why chrome leather may be adequately tanned and yet remain soft and flexible.

For cationic chrome tanning the bated skin is first pickled. The object is twofold; to bring the skin to a uniform, not too swollen condition on the acid side of the isoelectric point and to prevent too rapid tannage of the surface layers of the hide and unthorough tannage of the inner layers [slowing down of reaction (11-7b)]. The pickled hide is then treated in a revolving drum with the proper amount of chrome liquor, which is added slowly. Drumming is continued until tannage is judged complete. Some tannages do not reach completion until a small amount of alkali is added toward the end of the process.

After tanning, the skins are washed and a certain amount of oil or grease is added by drumming the leather in oil or a water emulsion of oil. This operation is called *fat liquoring*. Although the kind and degree of tannage have a great bearing on the shrinkage, tensile strength, and stretch of the final leather, the kind and amount of oil added also exert considerable influence on these same properties. Suppleness, water repellency, and resistance to flex cracking are increased. Oils also prevent wet leather from drying to a boardy condition.

The skins are finally dried to equilibrium with the atmosphere. Once chrome-tanned leather has been dried, it permanently loses its affinity for water.

Shoe uppers are made almost exclusively from chrome leather. It is strong and tough. Since its pores are not filled, it is flexible and soft and transmits water vapor so that the foot can "breathe" through it. Furthermore, when wet it will not dry out to a boardy condition.

1140. Vegetable Tanning. Tannin solutions are aqueous extracts of various woods, barks, nuts, roots, or leaves. Tannins are mixtures of complex polyphenols often containing also ester, ketone, carboxy, or other polar groups. In general, the more tannins in a solution, the greater its "astringency." The molecular weights of most tannins are probably 500 to over 2,000, and in the tanning solutions the dispersed particles are of colloidal size. Some tannins condense to higher molecular-weight particles ("reds") when acted upon by strong acids or oxidizing agents. It is a common behavior of phenols that they combine with many amines and amides to form crystalline products held together by secondary valence forces. This is especially true of the more complex phenols, and tannins give precipitates with pyridine, amides, and alkaloids. These facts serve as a basis for a satisfactory theory of vegetable tanning.

When animal skin is steeped in a tannin solution, tannins are deposited within the skin and the extensive property changes known as tanning occur. The capacity of the skin to take up tannins is very great, the voids in the hide becoming heavily loaded with material. Weight increases of over 300 per cent are possible.

The prepared skin from the beamhouse (usually bated) is pickled. The plumped skin is then steeped in a liquor ordinarily containing several different tannins. The first tanning liquor applied is weak and lacking in astringency. As tanning proceeds, *i.e.*, as the reaction between tannins and skin collagen advances, liquors of continuously increasing strength are applied until the desired degree of fixation is reached. This slow countercurrent treatment is essential to ensure tannage throughout—to avoid such rapid tanning and loading of the outer skin layers that diffusion into and tanning of the interior are prevented.

The tanned skin is then dried slowly. At the end of the drying process the grain surface, dense to begin with, is so heavily loaded that the voids are completely filled. This solid wall is brittle and cannot flex without cracking. To overcome this, the leather is dipped into warm water and then for a short time into warm dilute alkali, which removes some of the acidic tannins by dissolving them. The skin is then washed, neutralized, and again washed. Since the surface layer becomes lighter in color during this treatment, the operation is called *bleaching*. Before final drying, oil is introduced by fat liquoring, swabbing, or both. Because it is so heavily loaded, vegetable-tanned leather does not shrink on drying to the same extent as chrome leather.

Vegetable-tanned leather may be of two general kinds, one typified by belting, in which flexibility and tensile strength are paramount, and the other by sole leather, in which maximum abrasion resistance and stiffness are secured even at the sacrifice of some tensile strength. Therefore, to make belting, one adds enough acid to the prepared skin from the beamhouse operations to neutralize the lime but not enough to plump the hide extensively. Furthermore, while the skin is tanned thoroughly, it is not loaded to the limit. In this way the finished leather is left with a large amount of hide fiber per unit cross section, giving high tensile strength plus enough porosity to ensure flexibility and stretch rather than stiffness. By contrast, the skins for sole leather are treated with sufficient acid to cause a high degree of swelling and are then very heavily loaded.

Vegetable tanning blocks off polar (basic) groups of the skin. The secondary valence bonding between phenolic and other acidic groups of the tannins with basic groups of the collagen is strong. The leather is also heavily loaded, and there is a large effect on mechanical properties

traceable solely to this factor. Where chrome tanning more nearly resembles the vulcanization of rubber, vegetable tanning is strikingly similar to the improvement of rubber by the addition of reinforcing filler (Secs. 1310 *ff.*). For both rubber and leather the effective loading agent consists of particles of colloidal size with a high secondary-valence affinity for the loaded polymer. In both instances the product is stiffened, the plasticity reduced; tensile strength is increased, but elongation at break is reduced.

TEXTILE TREATMENTS

1141. After they have been woven or knit, practically all fabrics undergo various more or less standard *finishing operations* to make them more salable, attractive, or useful. Among these important operations are brushing, shearing, singeing, beetling, embossing, calendering, napping, bleaching, dyeing, sizing, and weighting. A whole industry called the *converting industry* is devoted to finishing, and a text specifically on textiles should be consulted for information on this subject.

For many years, natural and synthetic high polymers have been applied to fabrics in the form of continuous *coatings* to produce such items as artificial leathers, oil cloths, and tarpaulins, the fabric merely acting as a backing or support for the coating in question. In these treatments the appearance and hand are very radically changed, and the pores of the cloth are usually closed.

For garments and many other fabric uses it is often desired to modify certain properties such as crease resistance or water repellency without "closing up" the fabric or changing its hand or appearance. It is possible, by techniques applied mainly since 1930, to do just this. Modifying agents, most often polymeric, are applied that impart greatly enhanced resilience (crush and crease resistance), luster, shrink resistance, abrasion resistance, water repellency, etc. Many cloths are rendered "rainproof," spun rayons are given the resilience and crush resistance of wool, cottons the luster of silk, rayons the absorbency and coolness of linen. Appearance and color remain unaffected, and hand is very little changed or, in some cases, even improved. Millions of yards of fabrics are now so treated, and it is claimed by some that the art has been so highly developed that it is possible to modify fabrics as extensively by these treatments as by changing the kind of fiber used or by varying the twist of the yarn or the thread count, weave, or methods of converting the cloth. To be classified as truly effective, the treatment should not alter the original hand or appearance and should survive the repeated launderings or dry cleanings normal for the service life and intended use of the fabric.

1142. Polymerization of Resins within the Fiber. The essential features of one of the treating techniques are the following:

1. The fabric is immersed in an aqueous solution or emulsion of monomer, resinoid, or low-stage resin, which soaks into the fibers. (Polymerization catalyst is also added.)
2. Excess solution is removed by squeeze rollers. This is important since it is desired to avoid the subsequent formation of continuous coatings of resin on the surface of the fiber.
3. The fabric is dried at a relatively low temperature.
4. It is then heated for a short time at a temperature sufficiently high to cause the resin to polymerize *within* the fibers.
5. Washing and rinsing operations usually follow.

The specific effects produced depend on the kind of resin employed, its amount, and its distribution in the fiber. Resins that space-polymerize or react with the fiber molecules are particularly likely to survive laundering, dry cleaning, and wear. Different resins produce different effects on different cloths. Each type of fiber and fabric represents a separate problem and must be treated according to the results desired. Resins that are originally colorless and transparent and so stable to light, air, and aging that they remain thus for the life of the cloth are most suitable since they do not alter shades and colors.

The urea and melamine resinoids (Secs. 4437 and 1439) are extensively applied in the manner outlined above to improve abrasion resistance and resilience (crease and crush resistance). For example, in cotton sheeting and spun rayon dress fabric, with varying amounts of resin, resilience may be more than doubled, abrasion resistance increased as much as fivefold, and elongation at break increased or decreased by as much as 50 per cent, while shade, color, and appearance remain unchanged and hand is but little affected. The treated fabrics usually contain 10 to 15 per cent by weight of resin. A notable achievement was made with spun rayon. The resilience of this fabric was originally so poor as to impose serious limitations on its use. By resin treatment it was so greatly improved that its subsequent applications in suitings and dress goods marked an important development in the industry.

Other transparent resins, notably the acrylics, may be used. By varying the type of acrylic resin and its D.P., a wide variety of effects is obtainable. Usually the fabric contains only 2 to 3 per cent by weight of this resin. In many instances, prepolymerized acrylates requiring no curing step may be used. The importance of type of resin and type of fabric is indicated in Table 11-4. The acrylic resins may also be used for coating fabrics rather than impregnating the fibers. When so applied, they impart stiffness and gloss rather than resilience and abrasion resistance.

Another notable application of the technique under discussion has been

made in shrinkproofing wool. As discussed in Sec. 1133, wool exhibits an exaggerated tendency to shrink and felt into a hard inelastic mass during ordinary washing. A melamine resin treatment effects a startling reduction in this tendency. Partly methylated methylol melamines are used (Sec. 1439). The wool is immersed in and the fibers penetrated by a 2 to 15 per cent aqueous solution of the unpolymerized resinoids. Excess solution is then removed by passing the cloth through squeeze rolls to

TABLE 11-4. MODIFYING EFFECTS OF ACRYLIC-RESIN ON TWO FABRICS

Type of modifying resin	Fabric properties					
	Tensile strength, psi		Abrasion* resistance		Stiffness†	
	Cotton	Spun rayon	Cotton	Spun rayon	Cotton	Spun rayon
None. Control.....	131	121	3,000	2,000	2.0	2.0
Hard acrylate.....	132	128	10,000	3,000	4.0	4.0
Medium acrylate.....	130	141	9,000	5,000	2.8	3.6
Soft acrylate.....	121	134	15,000	4,000	2.3	2.1

POWERS, D. H., *Ind. Eng. Chem.*, **32**, 1543 (1940).

* Tested according to Tootal Broadhurst Lee standard; test piece rotated under a given load at high speed against a heavy worsted fabric of standard construction.

† Calculated on basis of the original fabric having a value of 2.0. The values are l^4/t ratios compared with that of the original fabric, where l is the distance between supports and t is the amount of sag of sample. A difference of 0.2 is detectable in touching the fabrics.

prevent coating effects. The fabric is then dried and the resin polymerized *in situ* at 230 to 300 F for 4 to 45 min. The process greatly reduces "relaxation shrinkage" and almost completely eliminates felting. Urea resins had previously been found to prevent shrinking and felting to some extent, but the effect was not maintained after repeated launderings. By contrast, at the end of 10 standard launderings (Federal Specification CCC-T-191a), a melamine-resin-treated wool showed a shrinkage of 3 per cent as compared with 43 per cent in an untreated control. The process does not entirely prevent shrinkage, but the improvement is so substantial that it unquestionably represents greater wear and serviceability to the consumer. Five or ten per cent by weight of resin in the fibers is sufficient for substantial shrinkproofing (Table 11-5); yet a fabric may contain as much as 15 per cent with no appreciable effect on hand or appearance. The resins are completely colorless and extremely stable to aging, acids, alkalis, and (dry-cleaning) solvents. It is also important that even 20 per cent by weight of the resin does not waterproof the fabric although swelling and water pickup are reduced by about

half. This means that the fabric can absorb water and be dyed and otherwise processed in the mill like untreated fabric. Furthermore, it can breathe. The reduction in shrinkage and felting appears to be due to a modification of the entire fiber and in this respect is fundamentally different from previous wool-shrinkproofing processes, which are characterized by a modification of the epithelial scales (Sec. 1133).

TABLE 11-5. EFFECT OF METHYLATED METHYLOL MELAMINE RESIN ON SHRINKAGE OF AN ALL-WOOL LIGHTWEIGHT FLANNEL

	% shrinkage after washing	
	15 min	60 min
Untreated control.....	11.1	29.2
2.5 % resin.....	4.2	12.5
5.0 % resin.....	2.1	5.5
10.0 % resin.....	1.4	2.4

JOHNSTONE, E. P., *Am. Dyestuff Reporter*, **33**, 310 (1944).

1143. Treatments with Cation-active Compounds. Many of the older finishing agents and dyes are *anion-active*. For example, in the case of sodium stearate it is the anion, $C_{17}H_{35}COO^-$, that is useful. The same holds for ordinary sulfated alcohol detergents, sulfonated oils, sulfonated amides, and most direct vat and sulfur dyes. The cation is usually the sodium or other metallic ion, and the active agent is the complex organic anion.

The term *cation-active* means simply that the useful part of a salt-type compound is the cation rather than the anion. Cation-active compounds are of more recent development commercially. They have proved highly effective as textile-treating agents, various kinds imparting permanent water repellency, permanent softness, and increased fastness of colored goods to laundering and perspiration.

At the current writing the most important cation-active agents for fabric modification are derivatives of ammonium hydroxide, particularly quaternary ammonium compounds, some of which are highly complex, with pyridine, quinoline, and other nitrogenous bases replacing the hydrogens of the ammonium ion. They are substantive on cellulose and undergo actual combination with cellulosic fibers. Their application involves the following steps:

1. Impregnation of the fabric by an aqueous solution of the treating agent at relatively low temperature
2. Quick drying at moderate temperature

3. Heating or "curing" for a few minutes at high temperature

4. Washing and rinsing

Since a cation-active compound will mutually precipitate an anion-active material, the fastness of many dyes to laundering and perspiration may be enhanced by an after-treatment with a cation-active agent.

Another valuable application is for rendering fabrics water-repellent. It is helpful to consider some general aspects of this subject before considering the cation-active agents in particular.

Fabrics may be either waterproof or water-repellent. Waterproofing is effected by coating the fabric with rubber, drying oil, or resin, which covers the fibers and also closes the pores of the cloth. Hand and appearance are changed radically, and the passage of air, moisture, or liquids is prevented. The fabric can no longer breathe. Although ideal for many purposes, this procedure has obvious disadvantages for certain clothing and household textiles.

The distinguishing characteristic of a water-repellent cloth is that it sheds water but still retains its porosity. Air and perspiration vapors can pass through the fabric so that body comfort is maintained. The older water-repellent treatments, such as the original cravenetting process, consisted in impregnating the fabric with hydrophobic metallic soaps, usually of aluminum or lead. In a later process a wax and aluminum soap emulsion was applied to the fabric. These treatments are not very satisfactory in that the repellency decreases with wear of the garment or is practically entirely removed by laundering or dry cleaning.

By treating cellulosic fabrics, silk, or mixtures of these fibers with a cation-active agent whose cations contain long-chain organic hydrophobic radicals, the fabric is rendered water-repellent. Hand, appearance, and color are virtually unaltered. The repellency effectively survives normal laundering and dry cleaning. Nonoily spots or stains may be sponged off with a damp cloth. The fabric resists absorption of perspiration and wrinkling due to body or other moisture. This spot and perspiration resistance may mean less frequent laundering and hence longer service.

1144. Mercerization. When native cellulose is immersed in various solutions of strong electrolytes, permutoid addition compounds form. If the cellulose is regenerated from these compounds and then dried, it has its original composition but has changed to the hydrate modification (Sec. 527). A native cotton fiber has a kidney-shaped cross section and a natural spiral twist. Its surface is distorted by convolutions and intermicellar cracks so that it reflects light irregularly and lacks gloss or luster.

Mercerization is the production of lustrous cellulosic fibers by treating native fibers with a strong electrolytic swelling agent, usually sodium hydroxide. In commercial practice, cotton is mercerized by holding the

thread or cloth under tension while it passes through a bath in which it is immersed in a sodium hydroxide solution, about 18 to 28 per cent NaOH, at room temperature for 1 to 2 min, after which the reagent is promptly and completely washed out with water while the tension is maintained. The treated cotton has a pleasing silky luster, and this simple process is consequently of great technical importance.

If an unstressed cotton fiber is immersed in a mercerizing bath, two major dimensional changes occur. One is a 20 per cent shrinkage in length; the other is a large lateral swelling reflected by an almost fourfold increase in cross-sectional area. Such anisotropic swelling is to be expected in an oriented high polymer. During the swelling the preferential alignment of crystallites along the main fiber axis virtually disappears. The fiber changes from a flattened spirally twisted tube to a straight cylinder in which the central canal has been practically shut. Evidently the primary wall is not dissolved or ruptured. After the swelling agent has been washed out and the fiber has been dried, the cross-sectional area returns to essentially its original value but the cross section has changed permanently from a kidney shape to an ellipse. The 20 per cent shrinkage in length is also permanent.

From a practical standpoint, keeping the fibers or cloth under tension during the treatment has several advantages. Shrinkage is eliminated, a higher degree of luster is attained, and higher tensile strengths in the finished products result.

The luster of mercerized fibers is commonly attributed to a smoothing and regularizing of their cracked and convoluted surfaces while they are in the swollen, highly plasticized condition. It has been pointed out that the fibers become elliptical in cross section during the process; and it has been shown that, the more nearly circular the cross section, the higher the luster of cotton fibers regardless of whether they are unmercerized or mercerized with or without tension.

X-ray studies show that during mercerization the fraction of amorphous material increases at the expense of the crystallite fraction. If the process is carried out without tension, the degree of orientation of the crystallites decreases greatly. Both these effects tend to lower the cohesive forces in the fiber. However, when the mercerizing is conducted under tension, the degree of orientation is maintained or may even be increased. In the latter case the cohesive forces tend to increase. Under these conflicting influences, mercerization may cause either an increase or a decrease in the tensile strength. Increases of as much as 20 per cent have been reported for single cotton fibers. In a yarn, which is a gross mass consisting of many intertwisted fibers, tensile strength is also a function of the distribution of tensile load among the individual

fibers. During mercerization of a yarn the fibers are in a highly plasticized condition; and if the process is conducted under tension, rearrangement could well take place via slight slippage of one plasticized fiber past another in such a way that any subsequent tensile load would be borne more uniformly by a larger number of fibers (Sec. 908). This would tend to increase the tensile strength. In the light of this complicated situation, the conflicting statements in the literature on the effects of mercerization on tensile strength are not surprising.

During mercerization, cotton changes from the native to the hydrate cellulose modification and like all hydrate cellulose mercerized cotton is more hygroscopic, more readily penetrable by dyes, easier to hydrolyze, etc. How much of this is attributable to the increase in amorphous fraction and how much to the greater accessibility of the hydroxyl groups in the more open hydrate form (Fig. 5-37, page 211) is a moot question.

The complexity of the mercerization phenomenon is evident from the following data: At room temperature, if raw or ordinarily purified cotton fibers are immersed in caustic soda at concentrations of less than about 10 per cent, no change in x-ray diagram occurs; no swelling compound forms, and no conversion to hydrate cellulose (mercerization) takes place. At the same temperature, immersion in a 13 to 19 per cent solution leads to the formation of soda cellulose I. The x-ray pattern of native cellulose is completely replaced by that of this swelling compound; and when the swelling agent has been washed out, only the x-ray pattern of hydrate cellulose is found, *i.e.*, mercerization is complete. At concentrations of 20 per cent or more a different swelling compound, soda cellulose II, forms with a different x-ray pattern. However, upon washing and removal of the alkali the cellulose is found to be completely in the mercerized form. At concentrations of 45 per cent, *no mercerization occurs*, while, at 50 per cent, partial mercerization again takes place, *i.e.*, the treated fiber shows the x-ray pattern of both native and hydrate cellulose. A 10 per cent NaOH solution does not mercerize at all at 20 C but mercerizes partly at 0 C and completely at -10 C. This unusual state of affairs is represented in Fig. 11-12.

With cotton fibers that have been mechanically rubbed to damage the surface, ground to a powder, or subjected to either oxidative or hydrolytic degradation the regions of partial mercerization disappear. They are mercerized either completely or not at all. Also, the same fibers that are mercerized completely by a 15 per cent NaOH when no tension is applied may require a 35 per cent NaOH solution to mercerize them under high tension.

The results may be summarized as follows:

1. Mercerization requires the initial formation of a permutoid swelling

compound such as a soda cellulose, followed by conversion to hydrate cellulose.

2. The formation of soda cellulose is favored by low temperature. At high temperatures, native cellulose is the stable modification, hydrate cellulose the metastable. Hence low temperatures also favor mercerization.

3. Any restrictive force such as that exerted by the fiber cuticle or by externally applied tension hinders penetration of the swelling agent into the crystallites and hence tends to inhibit mercerization.

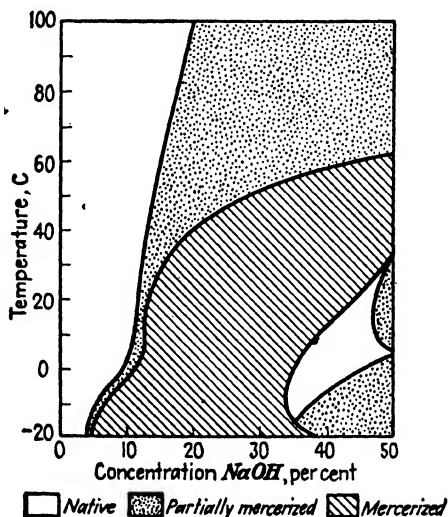


FIG. 11-12. Effect of temperature and concentration of sodium hydroxide on raw cotton. [W. A. Sisson and W. R. Sauer, *J. Phys. Chem.*, **45**, 717 (1941).]

One must not lose sight of the fact that the wall of a cellulose fiber is a *membrane* which is a two-phase system containing crystallites surrounded by amorphous material. The assumption that membrane phenomena are involved in mercerization helps to elucidate some of the effects.

The partial or complete lack of mercerization in the high-concentration low-temperature regions of Fig. 11-12 is difficult to explain.

1145. Other Fabric Treatments. Permanent water repellency may be imparted not only to fabrics but also to many other materials, both porous and nonporous, such as paper, brick, and glassware, by exposing them for a short time to gaseous silanes [Eqs. (2-1) and (2-2), page 39]. The adsorbed layer is extremely thin, invisible, and tactually undetectable so that appearance and hand are completely unaffected.

Silica is a high polymer. A water dispersion of a modified silica (particle size of about $0.06\ \mu$) has been discovered that, when applied to

fabric, both delusters the fibers and increases interfiber friction. The treatment is accomplished by simple immersion or sponging. The agent survives laundering or dry cleaning. Its delustering action eliminates "shine" from well-worn trousers, etc.

The tendency for rayon fibers to slip and cause dress fabrics to pull out at seams has been mentioned previously. In tire cord, slippage is often a greater cause of failure than actual breakage of fibers. Yarns containing very short staple fibers are inclined to shed these fibers. By increasing interfiber friction the silica treating agent minimizes or eliminates these defects.

There are a number of other important fabric-treating processes such as flameproofing, fireproofing, and mildew proofing. Works devoted specifically to textiles should be consulted for additional information.

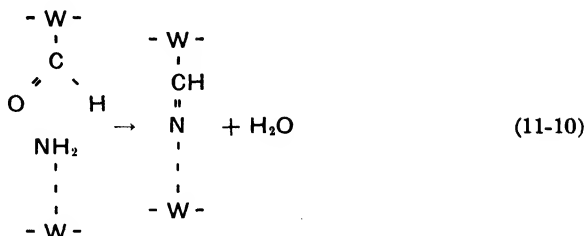
PERMANENT WAVING OF HAIR

1146. If a wool fiber is held under tension in steam for about 2 min and then while still under tension is removed from the steam and allowed to dry, it will remain in the stretched β -keratin form at almost double its original length even when the tension is released. But if the fiber is reimmersed and the tension then released while the fiber is still in the steam, it will supercontract to about two-thirds its original length. Presumably in the first instance it remains stretched because, when the water evaporates, salt bridging is reestablished and the fiber is "set" in the stretched condition. In the second instance, it presumably contracts because the salt bridges are temporarily weakened by heat and plasticizer, permitting the chain molecules to wriggle and fold to the supercontracted condition.

Human hair is a keratin fiber in many ways similar to wool. In accordance with the above, if it is dampened (plasticized with water) and wound firmly around a mandrel (curling iron) and the moisture is then driven out by heat, salt bridging is reestablished with the hair in the curled position and the curl is "set." This curl does not stay for long, especially on a damp day.

If the steaming experiment is repeated, this time by holding a stretched wool fiber in the steam for 2 hr instead of 2 min, not only does the fiber not supercontract but it is found to have suffered a *permanent* elongation, or set. This may be explained by assuming that steam first hydrolyzes the cystine cross-links [Eq. (4-52), page 152], enabling the molecules to straighten into a stretched position, and that this is followed by the formation of new cross-links, which "set" the once-freed chains into their new positions. One does not have to look far for possible new cross-links. Aldehyde groups formed in reaction (4-52b) could react with amino

groups of the wool as follows:



The Schiff's base linkages postulated in Eq. (11-10) would be stable under the experimental conditions.

Reaction (4-52) is promoted by alkali. Accordingly, in a "machine" permanent wave the hair is treated with alkali, wound around a mandrel, and heated. Permanent waves can also be given by room-temperature processes involving the breaking and making of cross-links by techniques similar to those indicated in Eqs. (4-50) and (4-53), pages 152 and 153.

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See also Appendix A.

PARTICULAR TOPICS

See references accompanying tables and figures of this chapter.

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CHAPTER 12

RUBBERS

In this and the succeeding chapter an attempt is made to present the best knowledge available at the time of writing and to by-pass as completely as possible older concepts of the rubbery state, which tend to confuse rather than to clarify.

GENERAL PROCEDURE FOR MANUFACTURE OF VULCANIZATES

1200. In order to appreciate the theoretical discussions that follow it is essential to have in mind the general operations involved in rubber-goods manufacture as well as some definitions and terms peculiar to the field.

Hevea-rubber hydrocarbon is originally taken from the tree in the form of an emulsion, *latex*. Synthetic-rubber hydrocarbons are also obtained mainly as latices from emulsion polymerizations; and while it is possible to manipulate these materials in their emulsion form by the technique known as *latex processing*, for various reasons a great portion of all vulcanized rubber goods is made in accordance with the following general procedure.

1. *Coagulation.* The rubber hydrocarbon is recovered from the latex by adding a coagulating agent, *e.g.*, acetic acid.

2. *Washing.* The resulting curds are partly freed of impurities by washing with water and squeezing out the aqueous serum by passing the coagulum through closely spaced rolls.

3. *Drying.* The resulting sheets of polyhydrocarbon are dried to remove water. Often bleaching agents and preservatives are added. The resulting crude, or raw, rubber is then ready for storage or eventual manufacture into finished goods. It should be noted that the nonhydrocarbon impurities left in the raw stock may exert powerful and important influences on the subsequent behavior of the material and the properties of the finished product.

4. *Mastication and compounding.* A raw rubber is unsuitable for all but a very few relatively minor applications. It is usually necessary to incorporate several compounding ingredients to improve mechanical or electrical properties, resistance to aging, resistance to solvents, etc. But in order to incorporate these ingredients smoothly and intimately it is essential to reduce the consistency of the tough, raw rubber to that of a

doughlike mass. This is commonly accomplished by drastic mechanical working on a roller mill or in a heavy-duty dough-mixing-type (Banbury) machine. This process is called *mastication*, *milling*, or *breakdown* and requires enormous power. It degrades the rubber, as evidenced by an increase in solubility and decrease in viscosity (Fig. 13-1, page 555). The rubber is transformed into a very weak mass into which other materials are readily mixed. Among the types of compounding ingredients that may be added are vulcanizing agents, accelerators, accelerator activators, aging retarders, loading agents, plasticizers, and coloring materials (Tables 8-1, page 311 and 13-7, page 566). These materials are most often finely powdered solids or sometimes pastes or viscous liquids.

TABLE 12-1. TYPICAL PROPERTIES OF A PURE-GUM (HEVEA) VULCANIZATE AND THE RAW RUBBER USED IN ITS MANUFACTURE

Property	Raw rubber	Pure-gum vulcanizate
Tensile strength, psi.....	300	3,000
Elongation at break, %.....	1,200	800
Permanent set.....	Large	Small
Rapidity of retraction (snap).....	Good	Very good
Hysteresis loop in load-elongation curve.....	Large	Small
Water absorption.....	Large	Small
Swelling in hydrocarbon solvents.....	Infinite (soluble)	Large, but limited
Tackiness.....	Marked	Slight
Useful temperature range.....	10 to 60 C	-40 to +100 C

At this stage the mass is so weak mechanically and so highly plastic that it is practically useless. If the rubber binder is nonvulcanizable, nothing much can be done about it. On the other hand, if it is vulcanizable, subsequent vulcanization or curing, which is akin to thermosetting, can more than make up for the damage caused by mastication and the finished vulcanizate may be remarkably improved even over that of the original unmasticated raw rubber.

5. *Preforming and assembling.* The doughy, highly thermoplastic unvulcanized mix often undergoes forming manipulations prior to vulcanization. Depending upon intended use, it may be calendered into sheets or extruded into tubing or rod. Belting and hose are made of rubber-fabric combinations. Tires contain metal (the bead) and layers of fabric and rubber. These items require preliminary assembly before they are ready for vulcanization.

6. *Vulcanization.* Vulcanization is usually, though not always, accomplished with the aid of heat and pressure. It converts the mix from a weak, mechanically useless thermoplastic mass to a strong, tough,

TABLE 12-2. EFFECTS OF VULCANIZATION AND CARBON-BLACK LOADING ON ELASTOMERS

Elastomer	Chemical nature	Unvulcanized			Pure-gum vulcanizate			Vulcanizate loaded with carbon black		
		400 ϵ_c "modu- lus,"* psi	Tensile strength, psi	Elonga- tion at break, ϵ_c	400 ϵ_c "modu- lus," psi	Tensile strength, psi	Elonga- tion at break, ϵ_c	400 ϵ_c "modu- lus," psi	Tensile strength, psi	Elonga- tion at break, ϵ_c
Hevea rubber (natural rubber)....	cis-Polyisoprene	..	355	1,200	400	3,000	700	2,500	4,500	600
Buta S (GR-S) (styrene rubber)....	Butadiene-styrene co- polymer	200	400	800	2,000	3,000	500
Buta N (GR-A) (nitrile rubber)....	Butadiene-acrylonitrile copolymer	200	600	2,500	4,000	600
Neoprene (GR-M) (chloroprene rubber).....	Polychloroprene	..	400	1,100	400	3,500	800	2,500	3,000	600
Thiokol A (thioplast).....	Polyethylene tetrasul- fide	450	300	300	1,500	1,500	500
Butyl rubber (GR-I) (isobutylene rubber).....	Isobutylene-isoprene co- polymer	300	3,600	1,000	1,000	3,000	400
Polybutene.....	Polyisobutylene	..	850	1,000	Nonvulcanizable	Nonvulcanizable	Nonvulcanizable	Nonvulcanizable	Nonvulcanizable	Nonvulcanizable
Polyvinyl chloride, unplasticized...	Polyvinyl chloride	..	5,700	2	Nonvulcanizable	Nonvulcanizable	Nonvulcanizable	Nonvulcanizable	Nonvulcanizable	Nonvulcanizable
Polyvinyl chloride, 30% plasticizer.	Polyvinyl chloride with external plasticizer	..	3,800	170	Nonvulcanizable	Nonvulcanizable	Nonvulcanizable	Nonvulcanizable	Nonvulcanizable	Nonvulcanizable
Polyvinyl chloride, 60% plasti- cizer.	Polyvinyl chloride with external plasticizer	..	1,000	500	Nonvulcanizable	Nonvulcanizable	Nonvulcanizable	Nonvulcanizable	Nonvulcanizable	Nonvulcanizable

Data from several sources, notably

WOOD, L. A., *Nat. Bur. Standards Circ.*, C 427 (1940).

FIRESTONE TIRE AND RUBBER CO., "Comparison of Physical and Chemical Properties of Rubber and Commercial Synthetics," 1940.

* Tensile stress at 400 per cent elongation. The term *modulus* to mean tensile stress at a certain elongation is unfortunate but is widely used in the rubber industry.

elastic, finished article. Some of the notable improvements consequent on this process are shown in Tables 12-1 and 12-2.

Among the techniques that have been successfully applied to natural and man-made rubbers are compression molding, transfer molding, injection molding, extrusion, blowing, dipping, and electrodeposition.

CLASSIFICATION OF RUBBERY MATERIALS

Owing to their high reversible extensibility, rubbery materials are often called *elastomers*. They may be classified in various ways according to source and characteristics.

1201. Natural Elastomers. Natural rubbers are obtainable from a considerable number of trees, shrubs, and vines mainly indigenous to the tropics. Usually the plant yields a milky latex, which is a more or less stable emulsion of polyhydrocarbon droplets in an aqueous serum. The stabilizing agents are naturally occurring proteins, soaps, and lipoids. From these latices there may be separated in each instance a considerable amount of rubbery polyhydrocarbons together with impurities, the latter constituting an integral and important part of the product. The bully tree (*Mimusops globosa*) yields ba'ata, the gutta-percha tree (*Palaquium gutta*) gutta-percha, the guayule shrub (*Parthenium argentatum*) guayule, and the Hevea tree (*Hevea brasiliensis*) caoutchouc, or Hevea rubber. These materials differ very considerably in their properties.

Because of its shape, type of bark, and adaptability to plantation production, together with the high yield and outstandingly excellent rubbery properties of its polyhydrocarbon, the Hevea tree has emerged as the main source of natural rubber. In normal peacetime before the Second World War, it supplied 99.5 per cent and all other sources 0.5 per cent; and, of the world's total supply of Hevea rubber, 98 per cent came from the Far East, 1 per cent was "wild rubber" from Brazil, the original home of the Hevea tree, and still smaller amounts came from Liberian and South American plantations. The war years witnessed an enforced scramble for other types of natural rubber, but the return of peace restored Hevea rubber to predominance. The unqualified term *natural rubber* is often used synonymously with Hevea rubber.

1202. Man-made Elastomers. Man-made elastomers were classified during the Second World War in accordance with the following definitions:

A *synthetic rubber* is a material obtained by chemical synthesis, possessing the approximate physical properties of Hevea rubber when compared in either the vulcanized or the unvulcanized condition. When vulcanized, it is capable of rapid elastic recovery after being stretched to at least twice its length at temperatures ranging from 0 to 150 F at any humidity.

A *substitute rubber* is a substance, made in whole or in part by a chemical process or from natural gums, resins, or oils, that in physical properties sufficiently resembles natural or synthetic rubber to replace either for particular purposes where only some and not all of the physical characteristics of natural or synthetic rubber need be supplied.

It will be noted that the foregoing distinctions between synthetic and substitute rubbers rest solely on physical and mechanical attributes. There is no precise line of demarcation, but in general the synthetic rubbers possess the more highly developed rubberiness.

It may be said that a rubbery material must almost necessarily be vulcanizable to approach the excellence of Hevea rubber. The most usual difference between synthetic and substitute rubbers is that the former are vulcanizable, while the latter are not.

Obviously, another method of classification would be division merely into vulcanizable and nonvulcanizable materials. Outstanding properties of various elastomers are listed in Table 12-3.

TABLE 12-3. COMPARATIVE PROPERTIES OF NATURAL, SYNTHETIC, AND SOME SUBSTITUTE RUBBERS

Elastomer	High-frequency electrical characteristics	Resistance to				Other characteristics
		High temperature	Aging	Outdoor exposure	Solvents	
Natural (Hevea) rubber.....	Good	Poor	Poor	Poor	Poor	
Buta S.....	Good	Good	Excellent	Fair	Fair	
Styrene rubber (more styrene than buta S).....	Excellent	Fair	Excellent	Fair	Poor	
Buta N.....	Poor	Good	Good	Fair	Excellent	
Neoprene.....	Poor	Good	Good	Excellent	Excellent	
Thioplast.....	Poor	Poor	Good	Excellent	Excellent	††
Butyl rubber and polybutene.....	Excellent	Poor	Excellent	Excellent	Poor	††
Polyethylene.....	Excellent	Poor	Excellent	Excellent	Excellent	‡
Silicone rubber.....	Good	Excellent	Excellent	Excellent	Fair	‡§
Polyvinyl chloride, plasticized.....	Poor	Poor	Excellent	Excellent	Fair	††

* Superior to all other elastomers with respect to tack, and ease of milling, compounding, extrusion, calendaring, and molding, and also with respect to reversible extensibility, resilience, and low heat-hysteresis losses. Hevea is still the standard to which all other elastomers are compared.

† Excellent gas impermeability.

‡ High ozone resistance.

§ Low-temperature suitability.

MOLECULAR STRUCTURE AND RUBBERINESS

1203. To be considered a truly good "rubbery rubber," a material must meet all the following criteria:

1. It must stretch readily and considerably under external tension (toughness and damping capacity).
2. It must possess a fairly high tensile strength and elastic modulus in the stretched state (strength).
3. It must retract rapidly (snap or rebound).
4. It must retract practically completely on release of tension (resilience and creep resistance).

This requires an exacting combination and balance of molecular, structural, and chemical characteristics. A basic requirement, by now obvious from previous discussion, is that, between the stretched aligned and the unstretched coiled states, the latter must represent the more stable condition of lower free energy.

The fundamental requirements for true rubberiness have been stated in Secs. 516 *ff.* What is needed is a mass of high-polymer chains for which the thermodynamically stable condition is coiled, tangled disorder. The molecular symmetry and flexibility and the intensity of the intermolecular forces of attraction must be such that, even if the chains be temporarily aligned or crystallized by external tension, they retract spontaneously to a disordered coil on release of the stress. The structure and chemical composition must be such that individual mers or chain segments can exhibit locally the rapid Brownian motions typical of small molecules in the true liquid state, but the chains must be long enough and tangled enough so that their long-range interaction impedes the displacement and Brownian movement of any single chain as a whole. Such a mass with its rapid *internal* Brownian movements and slow *external* Brownian movements will exhibit the "captive-liquid" behavior that is called the rubbery state. The mass, while possessing locally the properties of a liquid, will be enabled by the long-range interaction of the molecules to sustain moderate stresses and offer elastic resistance to any attempt at permanent deformation. The significance of these two types of Brownian motions will now be pursued further.

1204. Internal Mobility. We expect a rubbery material to stretch or deform under very low stresses and to possess a very low initial modulus of elasticity in the neighborhood of 15 to 150 psi. For this to happen, high internal mobility is necessary. Next we expect a stretched rubber to retract rapidly on release of the external tension. Here again a highly-developed local fluidity is required, since the *rate* at which individual chain segments will return from the higher free-energy configurations of

the stretched state to the lower free energy of their relaxed equilibrium state depends upon the rate of segment diffusion, *i.e.*, the rapidity of the internal Brownian movements. To summarize, in order to get a rubber possessing both ready extensibility and rapid retraction one must keep internal Brownian motion as rapid as possible. This condition is fostered by having inherently weak intermolecular forces of attraction, high chain flexibility, and poor chain symmetry.

1205. External Mobility: Fix Points. However, even if we provide local high fluidity, that in itself is not enough. The rubber will be very weak and, when subjected to sustained stress, will flow and undergo a large, undesirable permanent set. By the very aid of the rapid internal Brownian motion it will relax under stress into the extended rather than the contracted state, which is the case for an unvulcanized rubber. To prevent this, one must provide for long-range interaction and intermolecular "attachment" sufficiently strong to make the *external* Brownian movement (movement of whole chains past one another) so slow that no appreciable creep and permanent set occur within the time that the sample is in a stressed condition. In materials that meet the requirement of high local fluidity, secondary valence bridging, even in the crystalline stretched state, is too weak to prevent extensive molecular slippage. One must introduce a system of widely spaced *fix points*, *i.e.*, widely spaced points of strong chain anchorage. If this is properly accomplished, the material is a network of occasional fix points, joined by flexible molecular "ropes," that, though highly deformable under stress, returns to its original shape because of the restraining influence of these fix points. Although the internal local fluidity is essentially maintained, the external Brownian movement is practically eliminated. Tensile strength is increased, permanent set is reduced, and snap may be improved.

Fix points may be established in various ways. One is to introduce primary valence bonds, presumably sulfur, methylene, or oxygen cross-links, between the chains. Another is to introduce polar structures that are capable of establishing particularly strong secondary valence bridges. These may be salt bridges involving bimetallic ions, notably zinc. Either or both of the above types of fix points may be involved in the various processes known collectively as *vulcanization* (Sec. 1209).

Another method for introducing fix points is to incorporate very fine solid particles of high sorptive power such as carbon black. These presumably provide fix points, although weaker ones, by irreversibly sorbing parts of the chain molecules on their active surfaces. This technique is called *reinforcement*. In general, a sufficient *small* number of widely spaced *strong* fix points will accomplish the purpose, while preserving high local fluidity, better than a larger number of weaker fix points.

1206. Balance of Factors Required for True Rubberiness. Once these molecular concepts have been established, they constitute a working specification for producing good elastomers and point the way toward the improvement and modification of the properties of rubbery materials. If the intermolecular forces of attraction are too intense or the crystallizing tendencies too high, the local "viscosity" will be too high. Consequently, the material will be too rigid and, moreover, will creep back rather than snap back from the extended to the relaxed state. If the fix-point network is too tenuous or if the individual fix points are not completely stable but break down under stress, the material will undergo too much permanent set. On the other hand, if the fix-point network is too dense, the range of reversible extensibility will be decreased and, if carried to extremes, will eliminate local fluidity and result in a hard rubber, or ebonite. Also, too many fix points may seriously interfere with chain alignment and the even distribution of externally applied tension over the cross section of a stretched specimen, thus *reducing* the tensile strength (Sec. 909). Just how exacting are these requirements will be gathered from the following examples:

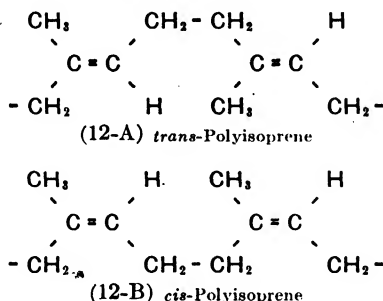
All polyhydrocarbon molecules are surrounded by inherently weak fields and are therefore basically suitable for rubberiness. In spite of this, polyethylene is not very rubbery. Polyethylene chains represent the *ne plus ultra* of architectural symmetry. The tendency to crystallize in small segments and the great number of hydrogen contacts in comparatively close packing preclude the fulfillment of the requirement of rapid internal Brownian movement. Also, the crystallized condition is so stable and the consistency so great that, when chain alignment occurs during stretching, the crystallized areas do not collapse on release of the external stress. In other words, the material does not retract. Its properties, therefore, are those more of a nonrigid plastic than of a rubber.

The purified hydrocarbons of Hevea rubber and gutta-percha are both polyisoprenes and are strikingly similar in many respects. The degrees of unsaturation are identical and the empirical formula is $(C_5H_8)_n$ in both cases. Yet, where Hevea rubber is highly extensible and rubbery, gutta-percha is relatively nonrubbery. If the two materials are fully hydrogenated, the resulting hydorrubbers are identical. The molecules must therefore be stereoisomers. Since each mer contains a double bond, cis-trans isomerism is possible.

Gutta-percha has a specific gravity of about 0.98, crystallizes readily, and has a melting point of about 60 C. A fiber period of 4.8 Å is prominent in the x-ray diagram. By contrast, Hevea rubber has a specific gravity of about 0.93. Even in the stretched crystalline state the specific gravity is only 0.95. Since its melting point is around 20 C rather than

60 C, it may be concluded that its tendency for the disordered state is greater. The fiber period is 8.2 Å.

It has been concluded that Hevea rubber is *cis*-polyisoprene while gutta-percha is composed of *trans*-polyisoprenes.



Molecular models are instructive. They show that a molecule built of *trans* units can straighten into a streamlined β -gutta-percha chain which can pack closely with neighboring chains into a dense material

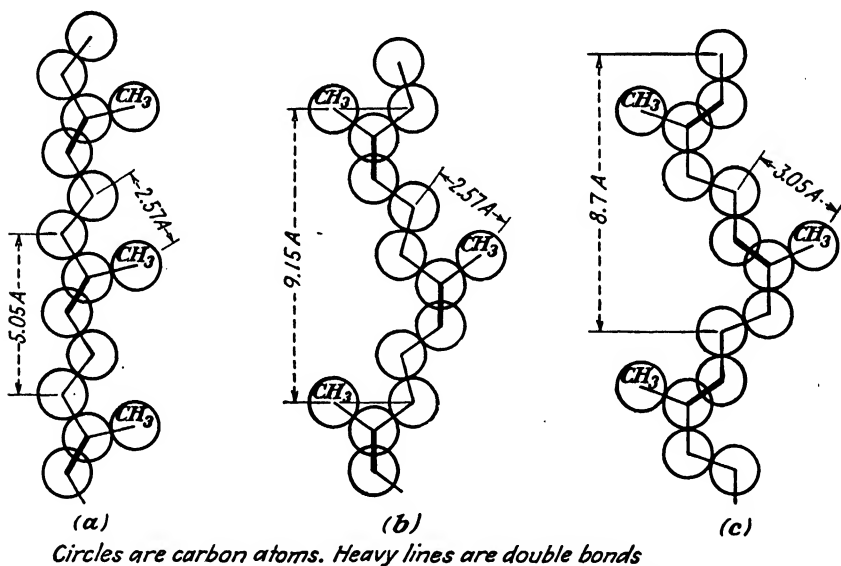


FIG. 12-1. Polyisoprene structures. (a) Gutta-percha, β -*trans*-polyisoprene. (b) Hevea rubber, *cis*-polyisoprene. (c) Gutta-percha, α -*trans*-polyisoprene. (H. Mark in "Chemistry of Large Molecules," Burk and Grummitt, editors, Interscience Publishers, Inc., New York, 1943.)

(Fig. 12-1a). On the other hand, a chain of *cis* units is decidedly kinked even in its most extended position (Fig. 12-1b); and although excellent orientation and crystallization can occur upon stretching, the chains cannot pack into as dense a structure as the *trans*-polyisoprene chains.

Furthermore, it is probable that the *cis*-polyisoprene chains are not planar and that the normal valence angles are slightly distorted when the material crystallizes, the crystallites being thus rendered relatively unstable so that they collapse promptly on release of tension. Thus, it will be seen not only that the requirements for highly developed rubberiness are very exacting but also that current theory is essentially in accord with the facts and accounts satisfactorily for the marked differences in rubberiness between two such chemically similar substances. Additional evidence for the general theory is provided by the effect of vulcanization on gutta-percha. Whereas before curing it is relatively stiff and nonrubbery, afterward it is very similar to vulcanized Hevea rubber. This may be attributed to the reduction of chain symmetry produced by the cross-linking and cyclizing reactions which probably occur during vulcanization.

BASIC METHODS FOR ATTAINING RUBBERINESS

It is instructive to discuss the basic techniques for attaining rubberiness in the light of the theoretical picture elaborated in the previous section.

1207. External Plasticization. A linear high polymer whose polarity, symmetry, and chain flexibility are such that it is normally classified as a plastic at room temperature can have its physical properties downwardly revised by external plasticization to the point where it is pliable and extensible and has high damping capacity (Table 3-2, page 84 and Fig. 3-4, page 83). However, the plasticized mass will not possess the snap, resilience, and high reversible extensibility of a true rubber. In terms of the previous discussion, external plasticization imparts local mobility but does not change the inherent flexibility of the chain molecules or supply the strong, widely spaced fix points so conducive to rapid retraction and resistance to permanent set under stress. In other words, the material possesses a pseudo rubberiness and falls into the category of substitute rubbers. A better term is *nonrigid plastics*. For applications where high resilience and reversible extensibility are not required such materials are often quite satisfactory. Many plasticized vinyl polymers may be used in this fashion.

1208. Internal Plasticization. Internal plasticization, notably by copolymerization, is an effective means of preventing crystallization and producing rubberiness from a combination of monomers each of which polymerized alone would be either a poorer elastomer or no elastomer at all. Offhand it might seem that the best way to arrive at true rubberiness is to build up very unsymmetrical copolymers, which, even at extreme elongations, are incapable of forming crystallites, but this is not the case.

As between two materials that meet the basic requirements of high extensibility and rapid retraction, a rubber whose chains crystallize

or close-pack at high elongations will, in general, be found superior to one whose chains do not. The reason is not difficult to find. Stress-induced crystallization at high elongations leads to increased intermolecular attractive forces, thus rendering the rubber self-reinforcing and contributing to high tensile strengths in the stretched state (Fig. 12-9, page 543). It is necessary only that the crystallites formed during stretching be not too stable so that they collapse promptly on release of the stress, thus permitting rapid retraction.

1209. Vulcanization. Goodyear discovered that noteworthy improvements in properties such as are listed in Table 12-1, page 511, could be brought about by heating Hevea rubber with small amounts of sulfur. (Small amounts of sulfur cause the formation of soft vulcanizates. Large quantities of sulfur result in hard rubber, or ebonites.) Appropriately enough, he called this process *vulcanization*. It has since been discovered that neither sulfur nor heat is indispensable to effect these changes. Hevea rubber in solution or in thin sheets may be similarly improved by soaking in sulfur chloride at room temperature. Selenium, tellurium, organic peroxides, and nitro compounds may be used in place of sulfur. (The common characteristic of these materials is that they all may act as oxidizing agents.) Sulfur does not vulcanize neoprene, but zinc oxide does. Under some conditions, neoprene is self-vulcanizing, requiring no specific addition of a vulcanizing agent to bring about the physical changes in question.

There are several points to consider. First, there is no one vulcanization reaction or process. Second, no matter how the physical changes in question are brought about, they seem to be accompanied by and associated with chemical reactions. Unfortunately, however, these reactions are so complicated that despite intensive study they are still imperfectly understood, and there is at the current writing too little quantitative correlation between the chemical aspects of vulcanization processes and the physical changes that accompany them. One is thus immediately confronted with the necessity of defining what is meant by vulcanization in order to avoid obfuscation of subsequent discussion. To this end, one is practically forced to a physical rather than a chemical definition, *viz.*, vulcanization (to produce a soft vulcanizate) is any treatment that decreases the thermoplasticity and increases the ultimate tensile strength and resilience while substantially preserving the high extensibility of an elastomer. The bulk of present experimental evidence indicates strongly that vulcanization is attributable to the formation of widely spaced fix points in the form of primary-valence cross-links, strong ionic bridges, or both. Although most of the discussion of vulcanization presented in this text is based on the working theory that primary valence bonding (space polymerization) occurs, at the current writing it is by no

means certain what the precise state of affairs is when rubber is vulcanized by heating with sulfur, organic accelerator, and a metal oxide such as zinc oxide.

REINFORCEMENT

1210. Definitions. For many heavy-duty items such as belting and tire treads, even properly vulcanized rubber does not possess sufficient tensile strength, stiffness, or resistance to abrasion and tear. These properties may often be considerably enhanced by incorporating before vulcanization sundry finely powdered fillers called *loading agents*, the resulting vulcanizates being known as *loaded stocks*. In distinction, an unloaded product is called a *pure-gum vulcanizate* (Table 13-7, page 566). Pure-gum vulcanizates are relatively soft, pliable, and extensible and are particularly suitable for such items as gloves, special laboratory tubing and stoppers, and rubber bands.

Some loading agents such as barytes and gilder's whiting do not enhance mechanical properties but are added to render a mix more manipulable during preforming or merely to cheapen the unit cost of the compound. These are termed *inert fillers*. Others such as carbon black may notably increase tensile strength, tear resistance, abrasion resistance, or all three. These are the so-called *reinforcing fillers*. Table 12-2 shows some effects of vulcanization alone and vulcanization plus carbon-black loading on several elastomers. It illustrates how important reinforcement can be. (See also Table 13-8 and Figs. 13-7 and 13-9, page 568 ff).

1211. Mechanism of Reinforcement. The mechanism of reinforcement is still incompletely understood. It appears likely from present knowledge that reinforcement does not occur unless there are strong surface forces acting between the filler and the rubber binder. There is evidence that a reinforcing filler orients itself in the mass when a loaded soft vulcanizate is stretched, whereas no such orientation occurs when the filler is inert. One fairly plausible theory is the following:

If the surface forces are sufficiently strong, the filler particles sorb the rubber molecules at the surface, thus affording fix points of a sort. (These fix points are far more numerous and not so strong as those afforded by primary-valence cross-linkage.) The system is consequently stiffened. The system may also be stiffened because the rubber chains are partly "stretched" around the filler particles so that it is forced to work at a higher point on its stress-strain curve. Finally, the "viscosity" is increased because of the hydrodynamic effect (Sec. 715). However, there is little if any improvement in truly elastic response to external stress. By contrast, if the surface forces acting between the filler particles and rubber chains are of low intensity, even weak fix points will not be provided and when the rubber is stretched the chains will

"flow" around the filler particles much like a true liquid. Hence, the action exerted by the filler will be relatively minor. Additional evidence in this direction is furnished by the *retarded* solution and swelling in solvents of unvulcanized mixes loaded with fillers which strongly reinforce, and the lack of such action by those which do not reinforce.

Comparing reinforcement with vulcanization, available evidence indicates that in a well-vulcanized rubber there are a small number of permanent, widely separated fix points. Vulcanization therefore preserves high local internal mobility while at the same time efficiently increasing elastic response to external stress, reducing creep and thermoplasticity, and reducing equilibrium swelling and solubility. By contrast, reinforcement introduces a large number of weaker, nonpermanent fix points. Local internal mobility is greatly reduced. A stiffening action and, what is more important, an increase in the heat developed during cyclic stressing result. At the same time, reinforcement does not materially eliminate creep and thermoplasticity. However, reinforcement may enhance resistance to abrasion and tear to a degree not at all attainable by vulcanization. Thus, each has its own advantages, and the production of a heavy-duty rubber article of maximum service life often requires both vulcanization and reinforcement.

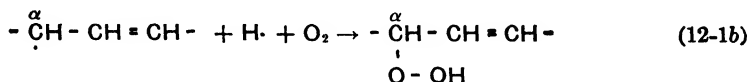
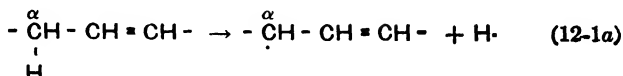
OXIDATION AND AGING OF RUBBER

1212. Saturated polyhydrocarbons such as polyethylene and polyisobutene are relatively stable. But buta S, buta N, and Hevea rubber are highly unsaturated and, like other olefinic compounds, are sensitive to heat, light, and oxidation. The attack by heat and light is much slower in the absence of oxygen.

The iodine number of Hevea rubber is around 370. Unless it is protected by aging retarders (antioxidants), it "ages." The total oxygen content increases slightly but unmistakably. The process is autocatalytic and is accompanied by serious physical deterioration. The rubber either becomes soft and sticky ("tacky") or hard, brittle, nonextensible, and easily cracked on flexing. The first of these changes is the sort one might expect from oxidative degradation. The second is the type that might accompany extensive cross-linkage. The particular deterioration occurring in a given sample depends upon conditions of stress, temperature, light, impurities, compounding ingredients, etc. In either case, the service life of the rubber is greatly reduced.

The mechanism of rubber oxidation is very complicated. Real progress toward its elucidation was not made till the 1940's through studies conducted on low-molecular-weight olefins. It has been shown, particularly by Farmer, that the primary step in the autooxidation of all olefins is the formation of peroxide groups, *not* at the olefin bond as for-

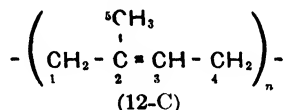
merly believed, but at α -methylene groups next to it where the hydrogen atoms appear to be particularly labile.



In other words, *loss of unsaturation is not an essential concomitant to the primary oxidative process of olefins as so long believed.* This is substantiated by the fact that loss of unsaturation does not follow oxygen uptake quantitatively.

The general efficacy of light and radical-producing catalysts in promoting this reaction and the ease with which it takes place in nonpolar solvents points to its dependence on free-radical formation.

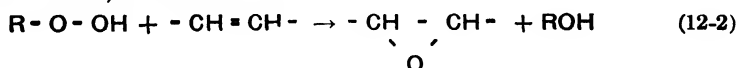
Substituents at the olefinic bond exert directive effects. Thus, in *cis*-polyisoprene (Hevea rubber),



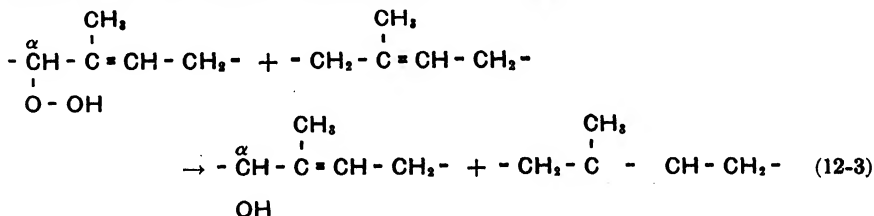
owing to the presence of the methyl group, peroxidation occurs more strongly at carbon 1 than at carbons 4 or 5 although it takes place at all three points.

In many olefins, including rubbers, decomposition of most of the original peroxide groups takes place side by side with new peroxidation, and a whole series of secondary oxidation reactions follows. The principal and least variable feature of these secondary autooxidative changes is that the hydroperoxide groups themselves revert to hydroxyl groups and the liberated active oxygen is consumed in oxidizing and saturating another olefinic bond with epoxide formation.

In general terms, this reaction is



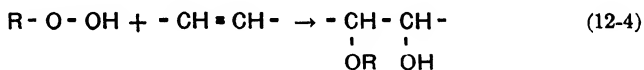
Applying this to Hevea rubber, one would have



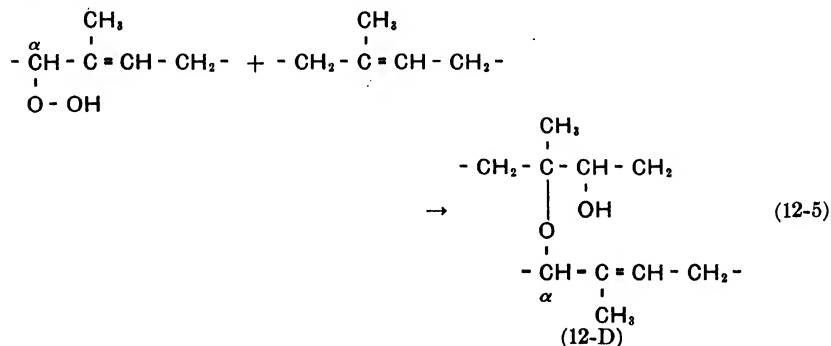
Epoxides are reactive, and the above stage is followed by further oxidation via several different mechanisms, which have not as yet been sufficiently disentangled to permit of precise statement. However, it is known that they may go so far as to cause chain breakage at olefinic bonds (oxidative degradation) or may saturate double bonds without rupturing them. In either event, oxygenated polar groups such as hydroxyl, carboxyl, carbonyl, and ether are left in the product.

Farmer's results with small molecules serve to explain the behavior of Hevea rubber and similar unsaturated polyhydrocarbons for which it has been shown that a very low over-all oxygen uptake is compatible with advanced oxidative degradation and loss of mechanical strength. Assuming an original molecular weight of 320,000 or more for Hevea-rubber hydrocarbon, the efficient utilization of molecular oxygen in keeping with the above mechanisms for autooxidation would permit the average molecular weight to be reduced by half when only a few hundredths of 1 per cent oxygen have reacted with the rubber. It is probably impossible to free a mass of raw rubber entirely of sorbed and entrapped oxygen. In light of this fact plus the complexity of the reactions and great inherent analytical-chemical difficulties, it is small wonder that all attempts to correlate stoichiometric oxygen uptake with its physical deterioration and aging have to the current writing met defeat.

In the reaction products from the autooxidation of low-molecular-weight olefins, Farmer also found oxygenated dimers, trimers, etc. In other words, *cross-linkage as well as degradation can take place during autooxidation*. The general equation for one of these polymerization mechanisms is

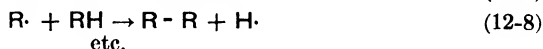


Applied to Hevea rubber this would be



This means that, during autooxidation, primary-valence vulcanizing cross-links can form in rubber with the loss of one double bond for each

oxygen cross-link formed. However, this is not the only type of cross-linkage possible. Working with low-molecular-weight hydrocarbons and benzoyl peroxide catalyst, Farmer found nonoxygenated as well as oxygenated low polymers (mainly dimers) in the reaction products. Benzoyl peroxide decomposes thermally to yield radicals $\text{C}_6\text{H}_5\text{CO}-\text{O}\cdot$ and $\text{C}_6\text{H}_5\cdot$ [Eq. (4-29a), page 120]. Above 100 C (commercial vulcanization) these attack an organic substance RH to form new compounds and radicals.



Reaction (12-8) is, of course, a polymerizing agency. When RH is an olefin, *e.g.*, cyclohexene, the main attack, according to Farmer, is substitution at the α -methylene positions [Eq. (12-6)]. But polymerization in accordance with reaction (12-8) also occurs.

These results serve not only to elucidate the changes accompanying the aging of rubber but also to afford a clue to the mechanisms of vulcanization reactions. Hevea and other olefinic rubbers undergo a non-sulfur vulcanization when heated with benzoyl peroxide. Furthermore, it is known that every autooxidizable substance capable of self-polymerization is polymerized to a greater or lesser degree by its own peroxides when undergoing oxidation. Also, since sulfur, selenium, and tellurium are rubber-vulcanizing agents, why not oxygen?

There has been a tendency to regard creep and relaxation as purely physical phenomena. However, in rubber vulcanizates these rheological properties can be explained in terms of the mechanisms of the chemical changes that occur during oxidation, *viz.*, chain rupture and cross linkage (Sec. 1333).

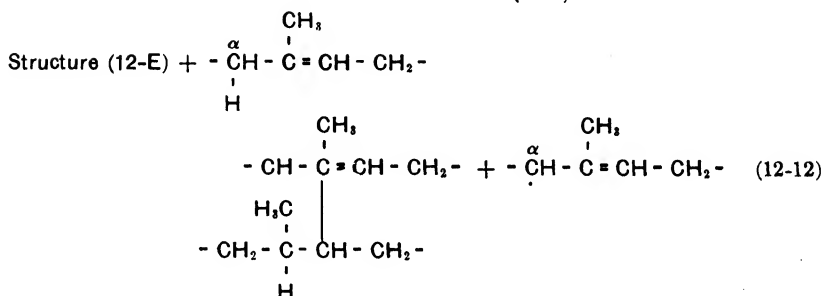
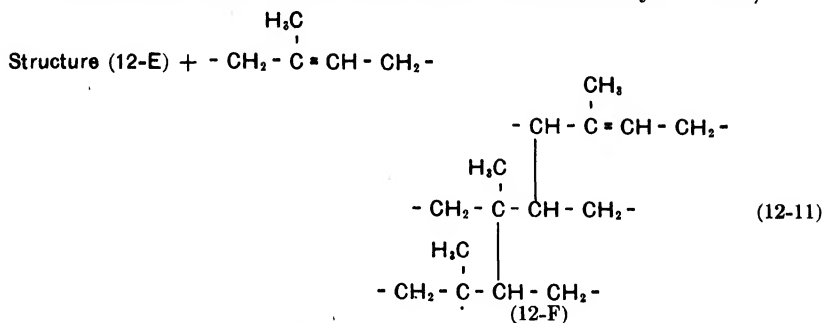
MECHANISMS OF VULCANIZATION

1213. Rubbers containing functional groups such as double bonds may be vulcanized by many reagents. The reactions may be grouped into two categories.

1. "Sulfur" vulcanizations in which the cross-linking agent is sulfur, selenium, or tellurium
2. Nonsulfur vulcanizations, which are accomplished by peroxides, nitro compounds, quinones, diaminobenzenes, etc.

The physical and mechanical changes accompanying these reactions can, in broadest theoretical terms, be attributed to primary-valence cross-linkage, very strong secondary valence bridging, or both. It has been demonstrated that Hevea rubber may be quite adequately vulcanized by adding polar Grignard reagents at the double bond of the

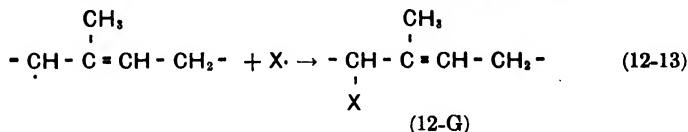
This process may then proceed further in several ways. Thus,



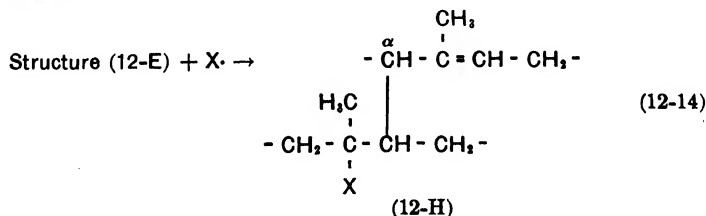
Reaction (12-11) is cross-linkage (vulcanization) while reaction (12-12) is chain transfer.

3. Termination of the reaction occurs when free radicals react with one another. This can take place either before or after cross-linkage but in any case results in the introduction of free-radical fragments on the rubber chains.

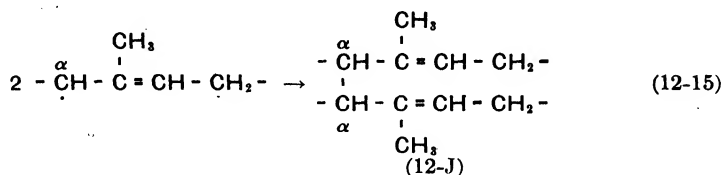
Thus, if the rubber free radical of reaction (12-9) interacts with radical X, termination results immediately and no cross-linkage takes place.



Termination after cross-linkage has occurred results from a similar reaction involving structure (12-E) or (12-F).



In the above theory, reaction of a rubber free radical with a second rubber free radical, leading to direct cross-linkage of two chains as shown in reaction (12-15), is rejected.

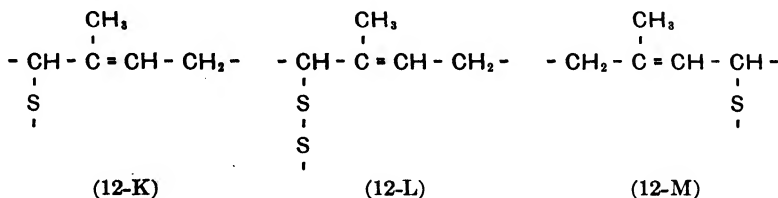


The probability of two such active centers being in effective position for reaction is low owing to hindrance in the highly viscous medium. The interaction between a rubber free radical and an electron of a double bond [Eq. (12-10)] is far more probable.

Upon applying the above generalization to the specific vulcanization of natural rubber with benzoyl peroxide it will be found to account satisfactorily for the facts as follows:

Benzoyl peroxide decomposes thermally at the vulcanizing temperature yielding radicals [Eq. (4-29)]. During the vulcanization, free benzoic acid forms [Eq. (12-9)]. The amount of unsaturation of the rubber decreases, and it is vulcanized [Eqs. (12-10) and (12-11)]. Benzoate groups are found in the vulcanizate [Eqs. (12-13) and (12-14)]. The rate of vulcanization is rapid, and after a very short time no appreciable changes in the chemical or physical properties of the vulcanizate occur. This is accounted for by the rapid decomposition of benzoyl peroxide at vulcanizing temperature and the usual rapidity of chain reactions.

1215. Sulfur Vulcanization. The mechanisms of sulfur vulcanization are still not so clear (Sec. 1209). However, convincing evidence has been brought forward that sulfide and disulfide cross-links exist between the chains of soft vulcanizates, these linkages being initiated mainly at α -methylene carbons, *e.g.*, structures (12-K), (12-L), (12-M).



This is only a partial answer. All the sulfur added does not react to form such linkages. There is no longer any reasonable doubt that several different rubber-sulfur reactions occur and that they vary with the accelerator employed. Examination of Fig. 13-3, page 560, shows that in the early stages of vulcanization the ratio of sulfur atoms reacted to double bonds lost is not constant but varies from 1 to 2 or more in different

For a system such as that under discussion it can be shown that the weight fraction of all molecules containing z chain sections (z finite) is given by

$$w_z = \frac{z^{z-1}}{z!} (\gamma e^{-\gamma})^z \quad (12-18)$$

where z is the *molecular complexity*, that is, the number of chain sections per molecule. In Fig. 12-2 the weight fractions of molecules composed of 1, 2, 3, 4, and 6 chain sections are plotted against γ . At all stages of the cross-linking process, w_z decreases rapidly as z increases; molecules unaffected by the introduction of cross-linkages ($z = 1$) are always present in greater quantity than any other species.

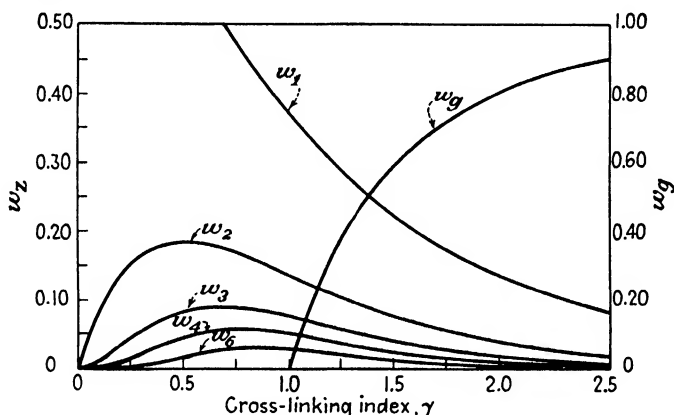


FIG. 12-2. Concentrations of gel and of molecular species composed of particular numbers of chain sections as functions of cross-linking index. [P. J. Flory, *J. Phys. Chem.*, **46**, 132 (1942).]

When $\gamma \leq 1$, all the molecules are *finite* size. Up to this point, no gel has formed, and all the molecules are soluble. When $\gamma > 1$, molecules of infinite size begin to form and gelation sets in. In complete analogy to systems containing trifunctional branch units there is a critical point, in this case $\gamma = 1$, which represents a gel point. *This critical point occurs when the number of cross-linkages is half the number of primary molecules.* Representing the weight fractions of sol and gel by w_s and w_g , respectively,

$$w_s + w_g = 1 \quad (12-19a)$$

$$w_s = 1 \quad \text{and} \quad w_g = 0 \quad \text{when} \quad \gamma \leq 1 \quad (12-19b)$$

Beyond the critical point, the system contains both sol and gel (Fig. 12-3), and it can be shown that

$$w_s = \frac{\gamma'}{\gamma} \quad \text{and} \quad w_g = 1 - \frac{\gamma'}{\gamma} \quad \text{when} \quad \gamma > 1 \quad (12-20)$$

where γ' represents the cross-linking index of the sol fraction alone.

As γ increases beyond unity, the composition of the sol fraction reverts over the same course traversed prior to gelation, γ' decreasing from 1 to 0. It can be shown that the cross-linking index γ'' for the gel fraction is given by $\gamma'' = \gamma + \gamma'$.

At incipient gelation, $\gamma' = \gamma = 1$, and $\gamma'' = 2$; that is, the cross-linking index for the gel fraction (present in infinitesimal amount) is twice that for the sol. After gel formation has started, introduction of additional cross-linkages not only increases the amount of gel but also

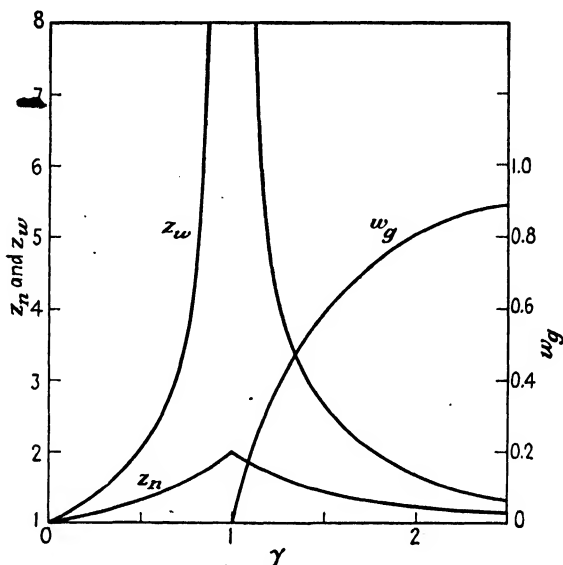


FIG. 12-3. Weight fraction of gel and other properties as functions of γ for a space-polymer system containing tetrafunctional branch units. The \bar{z}_n and \bar{z}_w curves beyond $\gamma = 1$ refer to the sol fraction only. [P. J. Flory, *J. Am. Chem. Soc.*, **63**, 3096 (1941).]

results in a preferential conversion of larger molecules to infinite networks, γ' decreasing while γ'' increases.

The cross-linking index is related to the weight fraction of sol by the convenient equation

$$\gamma = \frac{-\ln w_s}{1 - w_s} \quad (12-21)$$

By a procedure analogous to that applied to trifunctionally branched space polymers (Sec. 411), the number-average number of chain sections per molecule can be shown to be

$$\bar{z}_n = \frac{1}{1 - \gamma/2} \quad (12-22)$$

provided that no intramolecular cross-linking occurs. The weight-average

number of chain sections is

$$\bar{z}_w = \sum_{z=1}^{\infty} \frac{(\beta z/e)^z}{\gamma z!} \quad (12-23)$$

[Compare Eqs. (12-22) and (12-23) with Eqs. (4-24) and (4-25). The function $\beta(\gamma)$ is analogous to $\beta(\alpha)$ of the previous treatment.]

In this case, since the original chains are assumed to be of uniform size, \bar{M}_n and \bar{M}_w are, respectively, proportional to \bar{z}_n and \bar{z}_w . As in systems cross-linked by trifunctional branch units, the disparity between number-average and weight-average values is very great in the neighborhood of the critical point. As shown in Fig. 12-3, at the critical point, $\gamma = 1$, whereas \bar{z}_w is infinite, \bar{z}_n is equal to only 2. (Compare Fig. 12-3 with Fig. 4-5.) To summarize, in a space polymer composed of randomly cross-linked chains of *uniform length*, the behavior parallels that of trifunctionally branched polymers. Gelation occurs when the cross-linking index γ (equal to the number of structural units that are cross-linked per primary molecule) is unity, the number of cross-linkages is half the number of primary molecules, and the number-average molecular weight is twice that of the original primary molecules.

These equations make possible the quantitative evaluation of the degree of cross-linkage and the molecular weight of the chain sections in a vulcanized rubber. An important instance of their application is treated in Secs. 1221 ff.

1218. The Case of Long Chains of Randomly Distributed Length.

Most real polymeric products consist of molecules of mixed sizes, and a statistical treatment corresponding to the one just given but applicable to tetrafunctionally branched long chains randomly distributed (*i.e.*, to chains of which the size distribution is equivalent to that obtained by random coupling of bi- and tetrafunctional molecules) might be more useful than the restricted case of chains of uniform length. For such a system, it can be shown that the critical point is reached when $\gamma = \frac{1}{2}$ corresponding to $\alpha = \frac{1}{3}$ [Eq. (4-13)]. This is one-half of the critical degree of cross-linkage derived above for chains of uniform length; *i.e.*, gelation occurs when the number of cross-links is *one-fourth* the number of primary molecules. Thus, nonuniformity of chain lengths reduces the critical value for gelation.

In principle, such a treatment should be applicable to copolymer systems like styrene-divinylbenzene. In actual fact, however, it would be very difficult to apply since the coreacting monomers of most copolymerizations are not equally reactive and enter the copolymer chains in variable ratios that are not the same as their ratio in the initial mixture

(Sec. 427). Unless the ratio of coreactants actually entering the polymer chains were accurately known, quantitative application of statistical theory would be valueless.

MOLECULAR STRUCTURE VS. PROPERTIES OF RUBBER VULCANIZATES

1219. The phase changes occurring in rubber have been discussed in Secs. 516 *ff.* Below the first-order transition point ($\sim 25^\circ\text{C}$) the crystalline is the more stable form, and the unstretched material forms into randomly arranged crystallites, frozen rubber. Rubberiness is lost to a considerable extent. Below -73°C , the second-order transition point, even the ability of individual chain segments to rotate is lost, and rubberiness is entirely eliminated.

The x-ray photograph of unstretched Hevea rubber at room temperature is a diffuse halo characteristic of a high state of disorder. When the rubber is stretched, there is at first very little change; but at about 75 per cent elongation at room temperature the first vestiges of a spot pattern begin to appear, the pattern gradually growing sharper and more intense as the elongation is increased (Figs. 5-17 and 5-18*a* and *b*). (However, below 250 per cent elongation the extent of crystallization remains minor.) Concurrently, the intensity of the amorphous halo decreases, indicating that crystalline material is being formed at the expense of amorphous. At high elongations the structure is typically fibrous, the crystallite fraction becoming as much as 80 per cent. Upon retraction the amorphous halo is restored although there is a lag in the decrystallization process. A crystallization hysteresis loop is obtained, analogous to the load-elongation loop. Accompanying these changes in molecular arrangement with stretching, there are changes in the slope of the stress-strain curve as discussed in Sec. 723. Furthermore, the change from unstretched to stretched rubber is accompanied by an increase in density from about 0.93 to 0.95, and heat is evolved. Finally, molecular-weight measurements indicate that raw Hevea-rubber molecules are very long, the chains having an average D.P. of 1,000 or more, $(\text{C}_5\text{H}_8)_{1,000}$. Raw rubber is soluble in appropriate solvents and creeps under stress at a rapid, undiminishing rate.

This and other evidence indicates that raw Hevea rubber is composed of very long linear polyisoprene chains which are normally in a highly coiled and entangled condition and that tension extends and straightens the chains, an elongation of 1,000 per cent or more being attainable; but, despite the fact that this process is accompanied by crystallization, the chains re-coil and the mass retracts immediately upon release of the applied stress. Obviously, the amorphous condition is the more stable at room temperature (Secs. 231 to 233).

1220. Thermodynamic Properties of Rubber. In 1859 Joule discovered that rubber, in sharp contrast with metals and many other materials, evolves heat during elongation.¹ Little heat change occurs in the initial stages of extension; it begins roughly when the spot pattern appears in the x-ray photograph. It is generally accepted that this evolved thermal energy is heat of crystallization.

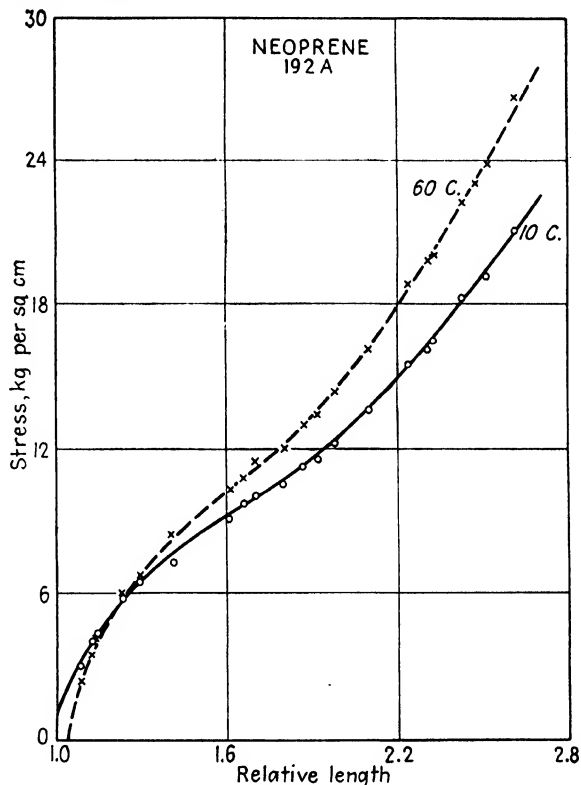


FIG. 12-4. Stress-relative-length curve for a neoprene at two temperatures. [L. E. Peterson, R. L. Anthony, and E. Guth, *Ind. Eng. Chem.*, **34**, 1349 (1942).]

It is further observed that, when a sample of stretched rubber is held at constant elongation, there is an *increase* in tension when the temperature is raised. This behavior is reflected in Fig. 12-4. Thermodynamically speaking, the Gough-Joule effect, *viz.*, increase of tension in stretched rubber with temperature, or the thermodynamically related temperature rise during adiabatic stretching, demonstrates that the extension of

¹ This discussion pertains to materials stressed within the elastic limit. When stressed or worked beyond this limit, *all* materials heat up owing to the irreversible conversion of work into heat.

rubber is accompanied by a definite decrease in entropy. The effect is encountered also in fibers, although to a lesser degree (Sec. 1116).

In 1932 it was first suggested that the retractive force in stretched rubber is due chiefly to the tendency for the chain molecules to return to the more probable (high-entropy) disoriented retracted configurations from the less probable (low-entropy) elongated and straightened configurations and that intermolecular attractive forces within the structure have little effect so long as no crystallization occurs. This has since been confirmed by experiments which show explicitly that until the onset of crystallization the change in internal energy with elongation is minor while the entropy increase is largely responsible for the retractive force, not only in Hevea rubber but in synthetics such as neoprene, buta S, and buta N as well.

The various statistical-mechanical treatments of Wall, Treloar, and Flory and Rehner yield the following relationships for a vulcanized rubber:

$$\Delta S = S(c) - S(1) = \frac{-k\nu}{2} \left(\alpha^2 + \frac{2}{\alpha} - 3 \right) \quad (12-24)$$

where α is the relative length l/l_0 [*n.b.*, per cent elongation = $100(\alpha - 1)$], l the length of stretched sample, l_0 the initial length of unstretched sample, ΔS the change in entropy in passing from the undeformed state ($\alpha = 1$) to the deformed state defined by α , k the Boltzmann constant, and ν the total number of chain sections.

The entropy contribution to the elastic retractive force may be computed directly from the above equation, and

$$f = -T \left(\frac{\partial S}{\partial l} \right) = - \frac{T(\partial S / \partial \alpha)}{l_0} = \left(\frac{kt\nu}{l_0} \right) \left(\alpha - \frac{1}{\alpha^2} \right) \quad (12-25)$$

where f is the retractive force and T the absolute temperature.

The tension τ (force per unit of initial cross-sectional area) is given by either

$$\tau = \frac{RT\nu}{V} \varphi(\alpha) \quad (12-26a)$$

or

$$\tau = \frac{RT\rho}{M_c} \varphi(\alpha) \quad (12-26b)$$

where ν is the number of chain sections in volume V , M_c the number-average molecular weight per chain section, ρ the density of rubber, and

$$\varphi(\alpha) = \alpha - \frac{1}{\alpha^2} \quad (12-27)$$

It has been shown by Guth, Mark, Treloar, Meyer, and others that isothermal stress-strain curves for both natural and synthetic rubbers are reasonably well produced by this function at elongations preceding the onset of crystallization (Fig. 12-5). They have also shown that the experimentally determined contribution to the retractive force of the change in internal energy on stretching is very small compared with the total tension (Fig. 12-6). This term has been neglected in the derivation of the above equations but does not alter the force-elongation curve

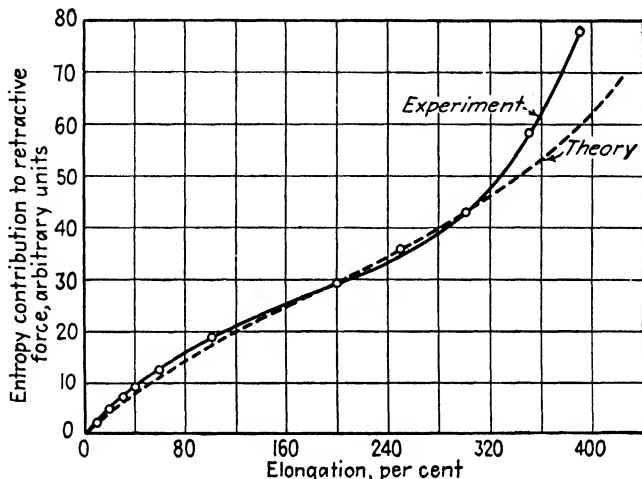


FIG. 12-5. Contribution of entropy change to retractive force as a function of elongation for a soft Hevea-rubber vulcanizate. [R. L. Anthony, R. H. Caston, and E. Guth, *J. Phys. Chem.*, **46**, 826 (1942).]

significantly below the region of crystallization. Equation (12-26) may be rewritten

$$\tau = G\varphi(\alpha) \quad (12-28)$$

The function $\varphi(\alpha)$ depends only on the length of the stressed specimen and is unaffected by the degree of cross-linkage or other structural factors. On the other hand, the parameter G , containing as it does ν or M_c , is definitely dependent upon the structure of the space polymer. It should vary with the molecular weight of the primary molecules and with the number of cross-links introduced during space polymerization.

Owing to the nature of $\varphi(\alpha)$, stress-strain curves of, for example, a set of rubber vulcanizates at different degrees of vulcanization made from the same kind of raw rubber should be of a common shape and should differ only in the factor G ; hence, the curves should be superimposable merely by altering the stress scale by suitable factors. This has been verified reasonably well for Hevea and butyl vulcanizates. In other

words, a single quantity, the stress at a given elongation (the tension "modulus"), is sufficient to characterize the stress-strain curve as a function of degree of vulcanization (extent of cross-linkage) except at higher elongations where crystallization occurs. However, the magnitude of the experimentally observed tension is somewhat larger than the preceding statistical equations predict (at least for butyl rubbers), and

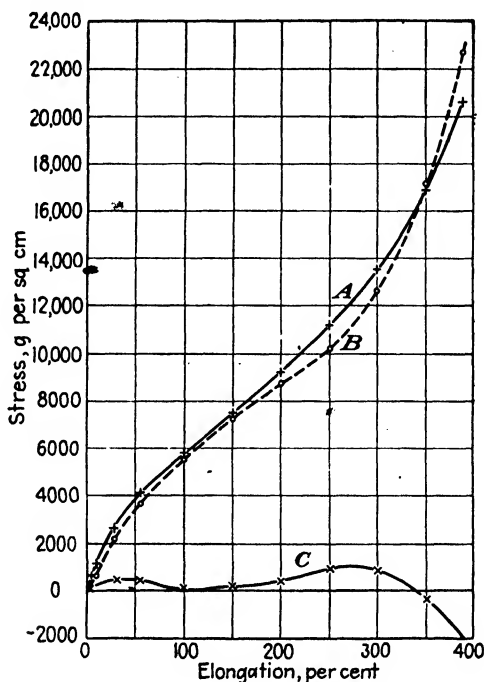


FIG. 12-6. Curve C: internal-energy contribution. Curve B: entropy contribution. Curve A: their sum, the total retractive force. These are all expressed as functions of corrected elongations for a soft Hevea-rubber vulcanizate at 20 C. [R. L. Anthony, R. H. Caston, and E. Guth, *J. Phys. Chem.*, **46**, 826 (1942).]

the tension varies less rapidly with the concentration of cross-linkages than the direct proportionality called for by the theory. What is most important, however, is that Eqs. (12-24) to (12-28) are derived on the assumption, direct or implied, that the primary molecules of the system are infinitely long. They do not take into account the molecular weight of the original primary molecules before cross-linkage has occurred; yet the properties of rubber vulcanizates exhibit a large dependence upon this factor (Fig. 12-9).

When a cross-linked rubber vulcanizate is immersed in a suitable liquid, it swells but does not dissolve. Equilibrium is eventually reached between the swollen solvated rubber and excess liquid. Often the volume

of the swollen rubber is five to ten times that of the initial dry volume. During swelling the chain sections are "stretched" so that this process is analogous to mechanical deformation with the difference that swelling occurs three-dimensionally. At the equilibrium point the gain in entropy representing further dilution of the rubber is balanced by the decrease in entropy that would accompany further distention (chain straightening) of the network.

The *equilibrium swelling ratio* (S.R.) is defined as the volume of swollen polymer at equilibrium divided by the volume of the dry polymer. By statistical treatment similar to that applied in developing the elastic relations, Flory and Rehner showed that, when the equilibrium swelling ratio is large, it should be approximately

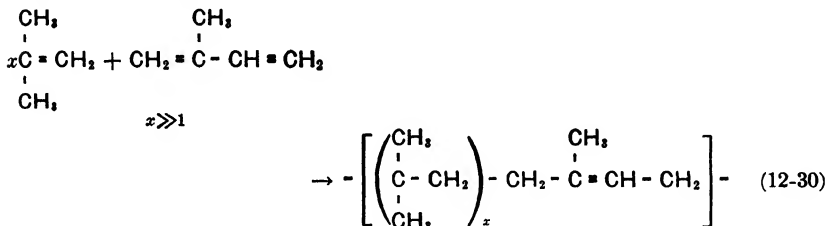
$$(\text{S.R.}) = \left[\frac{(1 - 2\mu)V}{2\nu V_A} \right]^{3/5} \quad (12-29)$$

where V_A is the molar volume of solvent and μ is a parameter characteristic of a given solvent-solute combination (Sec. 611). Equations (12-26a) and (12-29) indicate that there should be a definite correlation between the equilibrium swelling ratio and the retractive force accompanying mechanical deformation. However, as it stands, Eq. (12-29) suffers from the same shortcoming as Eq. (12-26): it does not take into account the effect of the molecular weight of the primary molecules from which the cross-linked network was built up. To overcome this fault, Flory extended earlier theory by reconsidering the structure of vulcanized rubber, taking into account the effect of the finite length of the primary molecules, the effect of "terminal chain sections" and other structural factors previously neglected. This important work, which afforded the first instance of a satisfactory quantitative correlation of the molecular structure of rubber vulcanizates with their physical properties, will now be outlined.

1221. Quantitative Correlation of Molecular Structure with Physical Properties. Until the late 1920's the only elastomers available were natural rubbers, and even until the 1930's the only one that had been intensively investigated was Hevea rubber. Naturally enough, but very unfortunately, all early studies of vulcanization and the correlation of molecular structure with the physical properties of an elastomer were attempted on Hevea rubber, a material completely unsuited for such investigations because of its susceptibility to complicated oxidation reactions and its considerable content of diverse nonhydrocarbon impurities. Consequently, there accumulated an enormous literature of variable and conflicting results and conclusions that hindered rather than fur-

thered the development of sound high-polymer theory. Flory's investigations were made not on Hevea but on butyl rubber.

Vulcanizable butyl rubber is made by low-temperature copolymerization of isobutene with small amounts (*e.g.*, 0.5 to 1 mole per cent) of a diolefin such as isoprene.



Such rubber is well suited to a study of the correlation of structure and properties. Among its merits are its simple, strictly linear chain structure. Careful studies have shown that the isoprene units enter the copolymer in the 1,4 position and are randomly distributed. Another feature is the ease with which the number of functional cross-linking olefin groups can be controlled by varying the amount of diolefin introduced during copolymerization. Furthermore, it possesses only about 1 per cent of the unsaturation of Hevea rubber, buta S, or buta N. Hence, its chemical stability is such that the operations necessary for separating experimental samples into fractions of narrow molecular weight (by fractional precipitation) can be carried out without oxidation, degradation, or other complicating chemical changes. Also, experimental batches may be milled and compounded without suffering appreciable breakdown, thus enabling one to preserve the initial structure and molecular weight of the sample up to the vulcanization step. [The susceptibility of Hevea rubber to oxidative and mechanical degradation is so great and it contains such an array of nonhydrocarbon impurities of unknown amount and composition that any similar investigation on this material is hopelessly complicated. Buta S, buta N, and other synthetics are similarly sensitive to oxidation and the situation is further complicated by their deviations from molecular-chain linearity (Sec. 430).] Other advantages of butyl rubber as an object of study are its ability to crystallize extensively at high elongations and its high ultimate tensile strength both with or without carbon-black filler.

1222. Flory's Theory of Vulcanized Rubber Structures. Flory's theory follows: If one starts with a mass of discrete, linear *primary molecules*, *e.g.*, unvulcanized rubber, and introduces cross-linkages at random points of contact, large molecules are gradually built up. According to statistical theory, infinite network molecules pervading the entire structure sud-

denly form when the cross-linking index γ reaches its critical value. If the original primary molecules are of uniform length, this occurs when γ just exceeds unity and the number of cross-links just exceeds half the number of primary molecules (Sec. 1217). As cross-linkage proceeds, more and more gel rubber forms at the expense of sol rubber.

Ordinarily, a finished soft rubber vulcanizate consists largely of gel. From a structural viewpoint, during the cross-linking process the original primary molecules have lost their identities. The basic element of the structure after cross-linkage and gelation is the *chain section*. Since the original primary molecules were of finite length, the chain sections of the vulcanizate are of two kinds, *principal chain sections*, extending between two points of cross-linkage; and *terminal chain sections*, extending from a cross-link to an untied chain end (Fig. 12-7). The number of principal chain sections depends upon the cross-linkage index. The number of terminal chain sections is twice the number of primary molecules. Since it is safe to assume that cross-linkage during vulcanization takes place at random, the terminal and principal chain sections are of the same average length. Furthermore, the weight fraction of the structure occurring as terminal chain sections also equals their "mole" fraction.

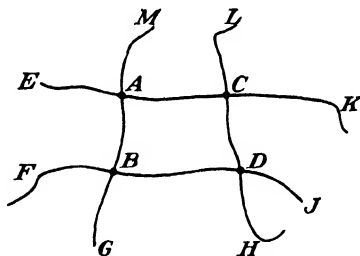


FIG. 12-7. Diagrammatic representation of vulcanized-rubber network structure showing principal and terminal chain sections. *EK, FJ, GM, and HL* are primary chain molecules (before cross-linkage). *A, B, C, D* are points of cross-linkage. *AB, AC, CD, BD* are principal chain sections (after cross-linkage). *EA, MA, LC, etc.*, are terminal chain sections (after cross-linkage).

Flory then postulated that, when the vulcanized rubber network is deformed as by stretching, only the principal chain sections are permanently oriented by the external stress and they alone contribute to the retractive force. A terminal chain section possessing, as it does, a loose end relaxes despite the stress and does not contribute to elastic resistance. It amounts to an inert flaw in the molecular network. The lower the molecular weight of the original primary molecules, the greater the relative number and concentration of these inactive terminal chain sections. Hence, *tensile strength and other properties of the vulcanizate depend upon the original molecular weight of the primary molecules as well as the degree of cross-linkage.*

According to Flory, another type of "flaw" is probably of outstanding importance in the network structure. Two or more chain sections, though not cross-linked to one another at any point, may be interlooped in such manner that they cannot become disentangled without rupture

of primary valence bonds, as, for example, chain sections AB and CD of Fig. 12-8. For purposes of discussion this phenomenon will hereinafter be called *permanent interlooping*. Such an interloop, in direct contrast with a terminal chain section, augments the elastic response to deformation, decreases swelling, and otherwise exerts effects similar to those of primary-valence cross-linkage. Terminal chain sections cannot undergo permanent

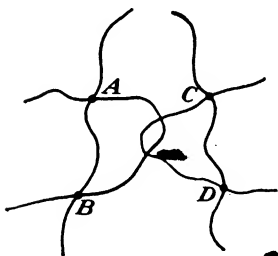


FIG. 12-8. Permanent interlooping of chain sections in a rubber vulcanizate.

interlooping, nor can permanent interlooping occur in unvulcanized uncross-linked masses. One should expect that, the longer the chain sections, the greater the relative contribution of permanent interlooping to the retractive force. In other words, an increase in retractive force arising from an increased degree of cross-linkage should be partly vitiated by an accompanying decrease in the interlooping factor.

The above concepts of vulcanizate structure are far more realistic than the assumption implied in the statistical derivation of Eq. (12-26), *viz.*, that the primary molecules are infinitely long and hence devoid of terminal chain sections.

If N is the number of primary molecules and ν_0 the number of cross-linked units, *e.g.*, cross-linked isoprene mers, the number of cross-links will be $\nu_0/2$ since there are two cross-linked units to each cross-linkage. Furthermore, the total number of chain sections will be $N + \nu_0$. The concentration of primary molecules (which have lost their identity after vulcanization) in moles per gram is

$$\frac{N}{\rho V} = \frac{1}{M}$$

where ρ is the density, V the volume containing N primary molecules, and M the molecular weight of the primary molecules. (If the primary molecules are a heterogeneous mixture, M should be replaced by \bar{M}_n .) Similarly, the concentration of cross-linked units is

$$\frac{\nu_0}{\rho V} = \frac{1}{M_c}$$

where M_c is the number-average molecular weight per cross-linked unit. Hence, the total concentration of chain sections in moles per gram equals $(1/M) + (1/M_c)$. The number-average molecular weight per chain section, M_c' , is the reciprocal of this quantity,

$$M_c' = \frac{1}{(1/M) + (1/M_c)} = \frac{MM_c}{M + M_c} \quad (12-31)$$

When $M \gg M_c$,

$$M_c' \cong M_c \quad (12-32)$$

Since, as previously pointed out, the weight fraction of terminal chain sections equals their "mole" fraction and there are two terminal chain

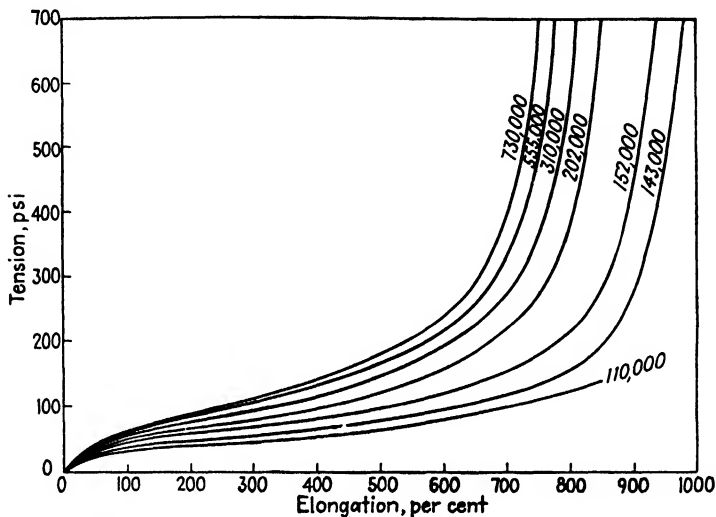


FIG. 12-9. Stress-strain curves for butyl-rubber vulcanizates made from low-unsaturation fractions of molecular weights indicated. [P. J. Flory, *Ind. Eng. Chem.*, **38**, 417 (1946).]

sections per primary molecule, it follows that the weight fraction of terminal chain sections, w_t , is

$$w_t = \frac{2(1/M)}{1/M_c'} = \frac{2M_c}{M + M_c} \quad (12-33)$$

and when $M \gg M_c$

$$w_t \cong \frac{2M_c}{M} \cong \frac{2}{\gamma} \quad (12-34)$$

where γ is the cross-linking index. The condition imposed on Eqs. (12-32) and (12-34) is met in all satisfactorily vulcanized rubbers.

Unfortunately, at the current writing no method is available for determining the number of permanent interloops.

Experimentally, the retractive force τ of a stretched vulcanizate is highly dependent upon M , the more so in the low-molecular-weight ranges (Fig. 12-9). Indeed, τ turns out to be far more dependent on M than upon M_c . This is immediately explained by Flory's theory, which takes into account the effect or rather lack of effect of the inert terminal chain sections, which should grow the more marked as the value of M decreases.

According to Flory the ν of Eq. (12-26a) should represent only those

chain sections which are active in offering elastic resistance to the externally applied stress and *not* the total number or concentration of chain sections. The effective number of chain sections is arrived at by the following reasoning: If the original primary molecules are of finite length, some of the cross-linkages are first required to combine the N primary molecules into one long, continuous molecule *devoid of circuitous interconnections*. This would require N cross-links (really $N - 1$ cross-links). Presumably this single, threadlike molecule would offer no particular resistance to an external stress. Only cross-linkages in excess of the number N would provide *internal* connections among different parts of the structure, effectively fixing it into a true network capable of elastic response to deformation. Then, since the *total* number of cross-linkages is $\nu_0/2$, the number of "effective" cross-linkages would be $(\nu_0/2) - N$; and since there are two chain sections per cross-linkage, the effective number of chain sections would be

$$\nu = \nu_0 - 2N = \nu_0 - 2\rho V/M \quad (12-35)$$

Upon substituting from Eq. (12-35) into Eq. (12-26), the retractive force becomes

$$\tau = \frac{RT}{V} \left(\nu_0 - \frac{2\rho V}{M} \right) \varphi(\alpha) = \frac{RT\rho}{M_c} \left(1 - 2\frac{M_c}{M} \right) \left(\alpha - \frac{1}{\alpha^2} \right) \quad (12-36)$$

where

$$\frac{RT\rho}{M_c} \left(1 - 2\frac{M_c}{M} \right) = G \quad (12-37)$$

the structural parameter. (If the original uncross-linked polymer were heterogeneous, M would have to be replaced by \bar{M}_n , the number-average molecular weight.)

Thus the simple factor $1 - (2M_c/M)$ expresses the dependence of retractive force upon M ; and, according to Eqs. (12-36) and (12-37), the tension moduli of vulcanizates produced from samples of the same unsaturation but differing in molecular weight should vary linearly with the reciprocal of M . Only in the unreal instance where M is ∞ does Eq. (12-36) reduce to Eq. (12-26b). Similar substitution in Eq. 12-29 yields

$$\left[\frac{1}{(\text{S.R.})} \right]^{3/2} = \left[\frac{2\rho V_A}{(1 - 2\mu)M_c} \right] \left(1 - 2\frac{M_c}{M} \right) \quad (12-38)$$

Combining Eqs. (12-36) and (12-38),

$$\tau = \frac{RT(1 - 2\mu)\varphi(\alpha)}{2V_A(\text{S.R.})^{3/2}} \quad (12-39)$$

i.e., the retractive force under tension should be inversely proportional to the $\frac{5}{3}$ power of the equilibrium swelling ratio.

1223. Quantitative Evaluation of the Degree of Cross-linkage. The preceding discussion indicates that it is essential to determine both M and M_c if the properties of rubber vulcanizates are to be related quantitatively to their structure.

A butyl rubber containing a known concentration of isoprene units was prepared by copolymerization of isobutene and isoprene. A series of raw rubbers, each of essentially homogeneous molecular weight (uniform chain length of primary molecules), was then prepared by close fractional precipitation (Sec. 614). These cuts therefore met the criterion of uniform chain length, thus making the statistical treatment of Sec. 1217 applicable. The molecular weight M of each raw fraction was determined viscometrically. By ozonolysis it was found that all the raw fractions of the series contained the same concentration of isoprene (potential cross-linking) units.

The raw fractions were compounded according to a standard pure-gum recipe and then vulcanized under constant conditions. All the vulcanizates consequently acquired the same concentration of cross-links, regardless of the value of M . The percentage of sol (soluble material) was determined on each vulcanizate and varied from about 1 per cent in vulcanizates made from raw fractions of the highest original molecular weight M to 100 per cent for those made from raw fractions of lowest M .

From statistical theory, incipient gelation and hence partial insolubility occur when an average of one cross-linked unit or one-half a cross-linkage is present per primary molecule. In other words, at the point of incipient gelation, $M_c = M$ and $\gamma = M/M_c = 1$. To obtain M_c it was only necessary to determine that vulcanizate of known M which is just completely soluble. The relation between γ and the weight fraction of sol is given by Eq. (12-21). To determine M_c it was necessary to fit the experimental data to the curve calculated from this equation and extrapolate to that critical value for which the weight fraction of sol in the vulcanizate is unity. Once M_c was thus located it applied to all the vulcanizates in the series, regardless of the original molecular weights of their primary molecules.

Two classes of butyl polymers were used, a "low-unsaturation" group containing about 0.5 mole per cent of diolefin and a "high-unsaturation" series with slightly over 1.0 mole per cent diolefin. (It should be noted that, even in the so-called high-unsaturation series, the concentration of isoprene units and hence the unsaturation are only 1 per cent of those of Hevea rubber.) The M_c values determined by the above method were

35,000 and 20,000, respectively. A molecular weight of 35,000 in the low-unsaturation polymers includes an average of 3.1 isoprene units or mers, from which it is concluded that only about 1 isoprene unit in 3 actually enters into cross-linkages. *The interesting conclusion is that no more than about 1 unit in 600 or more total monomer units need be cross-linked in order to vulcanize butyl rubber effectively.*

1224. Stress-strain Characteristics. The structural theory expressed by Eq. (12-36) was tested through stress-strain measurements. A series of butyl-rubber vulcanizates made from raw fractions of different molecular weights but constant amount of unsaturation yielded the experimental curves shown in Fig. 12-9. They illustrate not only the widely observed marked dependence of physical properties on the molecular weight of the primary molecules but also the common shape called for by the statistically derived Eq. (12-28) and its revised counterpart, Eq. (12-36). If each curve is transformed by merely altering its tension scale by a suitable factor, they may be made to coincide fairly well up to about 400 per cent elongation (no appreciable crystallization).

Equations (12-28) and (12-36) indicate that the stress-strain curve for a given vulcanizate (before crystallization occurs) may be characterized by a single parameter, either G or τ . The tension at 300 per cent elongation, τ_{300} , the so-called "300 per cent tension modulus," is plotted in Fig. 12-10 against $1/M$ for several sets of vulcanizates, each set being produced from raw samples of the same unsaturation (constant M_c) but varying molecular weights. This graph confirms the linear variation of τ_{300} with the reciprocal of M predicted by Eq. (12-36). Furthermore, from the straight lines of Fig. 12-10, M_c values of 37,000 and 26,000 are obtained for the same two series of polymers that yield estimates of 35,000 and 20,000 by the independent method described earlier. These values agree within the experimental error attendant upon either method and constituted excellent confirmation of the fundamental soundness of the theory.

When $M = \infty$, Eq. (12-36) reduces to Eq. (12-26b). Substituting the appropriate values into Eq. (12-36), the calculated intercept values for $M = \infty$ are considerably lower than those observed. Furthermore, Eq. (12-36) explicitly predicts that the modulus for $M = \infty$ should increase proportionally to the degree of cross-linkage, *i.e.*, inversely proportional to M_c . However, the high-unsaturation polymer represented by curve 1 of Fig. 12-10 contains at least 50 per cent more cross-linkages than the low-unsaturation polymers (curve 3), and yet its tension modulus extrapolated to infinite molecular weight is only 14 per cent greater. Flory attributes these real discrepancies to permanent interlooping. As previously stated, permanent interlooping acts like additional cross-linkage

and increases the tension value. Furthermore, its relative contribution to the retractive force should be greater, the longer the chain sections; that is, the discrepancies between the observed and calculated tension moduli should decrease as the degree of cross-linkage is increased. These expectancies are fulfilled in fact.

1225. Swelling Characteristics. Equilibrium swelling ratios in cyclohexane at 25 C were also determined for various vulcanized butyl fractions. Again the inverse linear dependence upon M predicted by theory

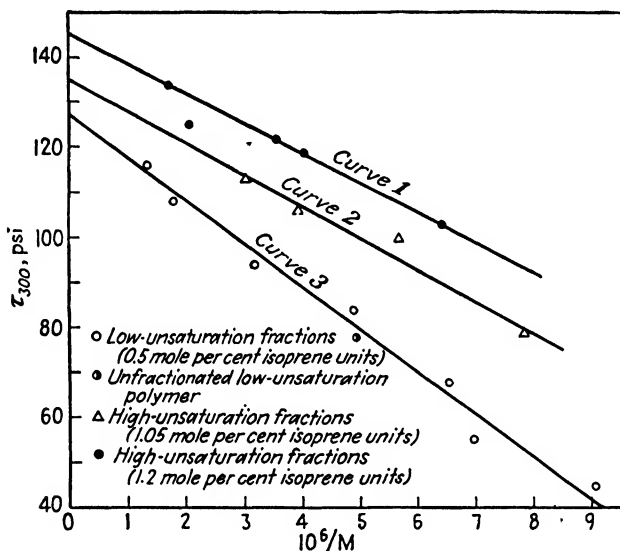


FIG. 12-10. Tension at 300 per cent elongation (300 per cent tension "modulus") of butyl-rubber vulcanizates as function of molecular weight, M or \bar{M}_n , of the rubbers before vulcanization. [P. J. Flory, *Ind. Eng. Chem.*, **38**, 417 (1946).]

[Eq. (12-38)] was experimentally confirmed as shown in Fig. 12-11. Values of M_c deduced from the straight lines of Fig. 12-11 yield values of 39,000 and 26,000 for the same two sets of vulcanizates for which 37,000 and 26,000 were obtained by analysis of stress-strain data.

The inverse relation between tension modulus and the $\frac{5}{3}$ power of the swelling ratio predicted by Eq. (12-39) was also satisfactorily confirmed as illustrated in Fig. 12-12.

This experimental confirmation of Eq. (12-39) affords evidence that the structural factors responsible for elastic retraction of a rubber vulcanizate are quantitatively the same as those which control the extent of swelling in solvent, *i.e.*, primary-valence cross-links and permanent interloops. Secondary valence bridging plays no important role since it would be overcome by the solvent causing swelling.

1226. Behavior of Heterogeneous Polymers and Influence of Nonvulcanizable Ingredients. During the course of the investigations it was found that, if the cross-linking index γ was sufficiently high to ensure the

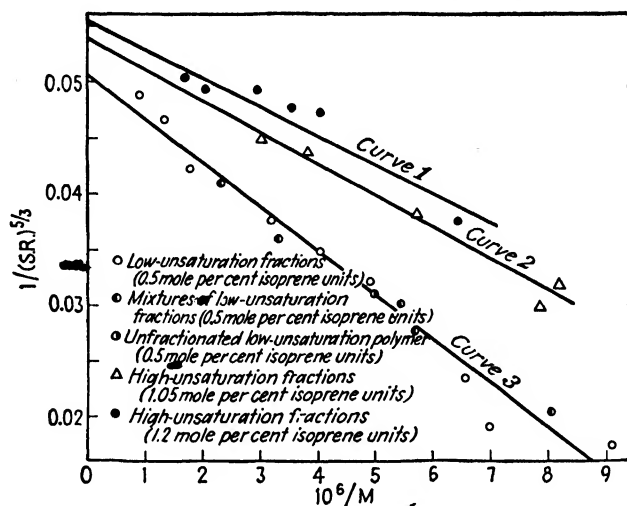


FIG. 12-11. Swelling ratio as function of molecular weight, M or \bar{M}_n , for butyl-rubber vulcanizates. [P. J. Flory, *Ind. Eng. Chem.*, **38**, 417 (1946).]

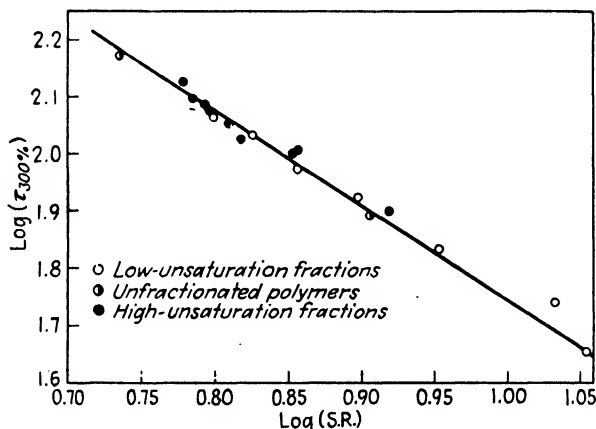


FIG. 12-12. Tension modulus at 300 per cent elongation as function of swelling ratio for butyl-rubber vulcanizates. (The straight line is drawn with the theoretical slope of $-5/3$ on the log-log plot.) [P. J. Flory, *Ind. Eng. Chem.*, **38**, 417 (1946).]

attachment of virtually all the original primary molecules into the cross-linked vulcanized networks, heterogeneous polymers of molecular weight \bar{M}_n have properties which coincide with those of homogeneous polymers of molecular weight M , provided that $\bar{M}_n = M$; i.e., the tensile strength is an explicit function of the number-average molecular weight and is inde-

pendent of the particular molecular-weight distribution (Figs. 12-10 and 12-11).

On the other hand, if a heterogeneous polymer contains molecules so small that they do not contain enough unsaturated units to become cross-linked to the gel network, these molecules act as soluble inert nonvulcanizable material that does not contribute to the tensile strength or limit swelling. These molecules must therefore not be counted in estimating the effective number-average molecular weight. By incorporation of saturated, nonvulcanizable material such as polyisobutylene into raw butyl rubber, it is found in confirmation that tensile strength in resulting vulcanizates is unaffected by the molecular weight of the inert "diluent" and depends only on the total amount present. In general, molecules that do not become cross-linked to the vulcanized network contribute nothing to the elastic resistance and indeed lower the ultimate tensile strength by interfering with the crystallization of the butyl-rubber network on stretching.

1227. Ultimate Tensile-strength Relations. For a rubber such as Hevea, neoprene, or butyl, whose molecules are symmetrical and hence capable of crystallizing extensively at high elongations, the stress-strain curve of a pure-gum vulcanizate made from it rises markedly at high elongations, the curve bending toward the stress axis. This self-reinforcement is undoubtedly attributable to the close packing and enhanced intermolecular attractive forces in the stretched state. In its highly stretched condition the structure of the vulcanizate resembles that of a fiber, and the ultimate tensile strength is high. By contrast, owing to copolymerization and the side reactions taking place during their synthesis (Sec. 430), buta-S and buta-N rubber molecules are so lacking in symmetry that they cannot crystallize appreciably even at high elongations. The ultimate tensile strengths of their pure-gum vulcanizates are low (Table 12-2, page 512).

Flory tested the following postulate: Only the principal chain sections of butyl vulcanizates are capable of permanent orientation on stretching; terminal chain sections, possessing a free end, relax into disordered coils even in the stretched state. Therefore, the ultimate tensile strength depends upon w_p , the weight fraction of orientable active or principal chain sections. From Eq. (12-33) it follows that

$$w_p = 1 - w_t = 1 - \frac{2M_c}{M + M_c} \quad (12-40)$$

If it is further postulated that the ultimate tensile strength varies linearly with the weight fraction of "active" chain sections, it follows from Eq. (12-40) that the tensile strength decreases linearly with $1/(M + M_c)$,

which is approximately $1/M$ if M is sufficiently large. (For heterogeneous molecules, \bar{M}_n should replace \bar{M} .) In Fig. 12-13 the ultimate tensile strengths of low-unsaturation butyl vulcanizates are plotted against $1/(M + M_c)$, the value of M_c being taken as 37,000. Surprisingly good accord with the postulated relationship is shown.

It turns out that for pure-gum butyl vulcanizates, at least, the highly complex property, tensile strength, is accounted for by a surprisingly simple structural interpretation, *viz.*, the ultimate tensile strength s_T is

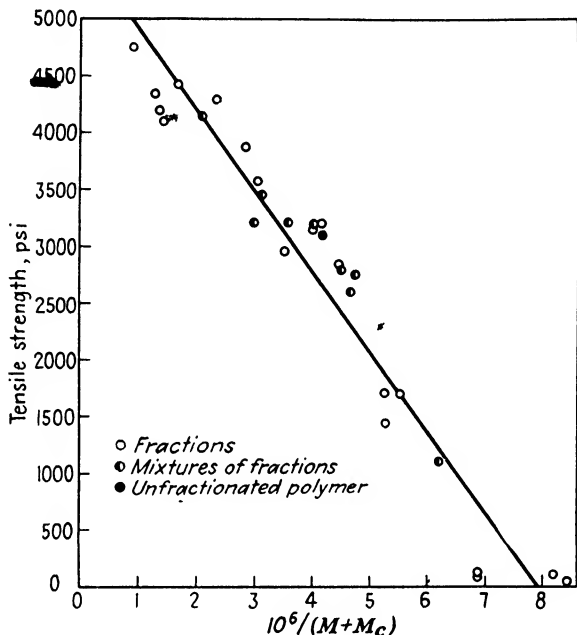


FIG. 12-13. Tensile strength as function of $(M + M_c)$ or $(\bar{M} + M_c)$ for low-unsaturation pure-gum butyl vulcanizates. [P. J. Flory, *Ind. Eng. Chem.*, **38**, 417 (1946).]

a linear function of the fraction of the rubber that is orientable under tension and depends directly on the degree of crystallinity attained at high elongations, *i.e.*, the percentage of orientable material that is actually oriented by stretching. In other words,

$$s_T = a(w_p - b) \quad (12-41)$$

where s_T is the ultimate tensile strength, a and b are constants, and w_p is the weight fraction of principal chain sections (in the absence of inert or diluent materials). It is probable that Eq. (12-41) will be found to apply to other stress-crystallizable rubbers such as Hevea, but it is doubtful whether such a relation would hold for noncrystallizing vulcanizates.

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See also Appendix A.

PARTICULAR TOPICS

See references accompanying tables and figures of this chapter.

Synthetic Rubber

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- BALL, J. M., "Reclaimed Rubber," Rubber Reclaimers Association, New York.

Reinforcement

- BRAENDLE, H. A., Chap. 18 in Vol. 6, "Colloid Chemistry," J. ALEXANDER, editor, Reinhold Publishing Corporation, New York.

Vulcanization

- Symposium on "Vulcanization of Rubber," *Ind. Eng. Chem.*, **31**, 1381-1406, 1455-1488 (1939).
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Molecular Structure and Properties of Rubbers

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CHAPTER 13

RUBBERS (*Continued*)

1300. Wood, stone, metals, fibers, and natural plastics such as clays have been available for many ages and have been fashioned into almost numberless artifacts useful or essential to our material well-being. By contrast, rubber is a new arrival. Just when a rubbery material was first applied to a useful mechanical purpose is not known, but it was not until 1770 that Joseph Priestley wrote, "I have seen a substance excellently adapted to the purpose of wiping from paper the marks of a black lead pencil. . . ." And it was not until Charles Goodyear's discovery of vulcanization in 1839 that rubber as we now know it came into existence. Vulcanization enormously enhances its useful properties and applications. One American company alone manufactures over 33,000 rubber items. It would be difficult if not impossible for modern industry to function successfully without rubber since it alone has the high reversible extensibility, toughness, resilience, and shock-absorbing capacity so essential to the operation of present-day high-power high-speed machines.

IMPURITIES IN RAW RUBBERS

Natural raw rubbers are agricultural products in the strict sense. Hence they contain complex mixtures of impurities in varying amounts. Hevea rubber is typical.

1301. Raw Hevea Rubber. Hevea-rubber latex as it is tapped from the tree is a milky emulsion of fine polyhydrocarbon globules in a watery serum. It contains proteins and soaps that stabilize the emulsion, as well as fatty materials, carbohydrates, and mineral matter. A typical analysis is shown in Table 13-1.

TABLE 13-1. COMPOSITION OF HEVEA-RUBBER LATEX

Item	% by wt
Rubber hydrocarbon.....	30-45
Water.....	65-50
Proteins.....	2
Soaps, fats, and related compounds.....	1
Carbohydrates.....	1
Inorganic matter.....	0.4
Specific gravity, 0.98	Analysis varies
pH (when fresh), about 7.0	with season,
Isoelectric point, 4.2	age of tree, etc.

From studies involving techniques of micromanipulation it has been shown that the Hevea-rubber globules possess a definite morphology. The particles are about $0.2\ \mu$ in diameter and contain three layers—a center consisting mainly of lower molecular weight sol rubber; over this, a skin of higher molecular weight gel rubber sufficiently strong to resist penetration by a needle; finally, an outermost sorbed layer containing mainly proteins and probably also soaps. The materials of the sorbed layer act as emulsifying agents, and their ionization imparts a negative electrical charge to the globules.

Most Hevea rubber reaches the compounder in the form of pale crepe or smoked sheet. These forms are made by coagulating the latex with acetic or formic acid and removing much of the serum from the hydrocarbon by water washing and squeezing through rollers. Pale crepe has been bleached. Smoked sheet is brown because of absorption of phenolic compounds during drying in a smokehouse. Some "whole-latex" sprayed rubber is used. It is made by evaporating the water from latex in a spray drier and contains all the solid impurities originally present. Typical analyses are shown in Table 13-2.

TABLE 13-2. COMPOSITIONS OF RAW HEVEA RUBBERS (PERCENTAGES)

Item	First latex smoked sheet		First latex pale crepe		Whole latex sprayed
	Average	Range	Average	Range	
Moisture.....	0.6	0.3-1.2	0.4	0.2-0.9	2.4
Acetone extract.....	2.9	1.5-3.5	2.9	2.3-3.5	5.5
Protein.....	2.8	2.2-3.5	2.8	2.4-3.8	4.5
Ash.....	0.4	0.2-0.9	0.3	0.2-0.9	1.4
Rubber hydrocarbon (by differ- ence).....	93.3	93.6	86.2
	100.0	100.0	100.0
Water extract.....	0.3	0.2	8.6

DAVIS, C. C., and J. T. BLAKE, "Chemistry and Technology of Rubber," Reinhold Publishing Corporation, New York, 1937.

The acetone extract contains powerful antiaging compounds. (Acetone extracted rubber oxidizes and deteriorates very rapidly.) It also contains components, notably fatty acids, that are accelerator activators. The protein fraction contains accelerators. The water extract includes salts, soaps, proteins, water-soluble fatty acids, and substances containing phosphorus. Copper and manganese compounds of the extract catalyze oxidative deterioration and adversely affect tensile strength and elastic moduli. The water-extract components increase water absorption and

seriously lower the electrical insulating properties of finished vulcanizates. They also render rubber difficult to masticate. Finally, it has been shown that even highly purified Hevea-rubber hydrocarbon contains 0.04 per cent oxygen present mainly in hydroxyl structures. These polar groups exert important effects on the viscosity and thixotropic behavior of rubber solutions, as discussed in Sec. 316.

To summarize, raw Hevea rubber is an agricultural product containing 6 to 10 per cent of nonhydrocarbons in highly variable amounts. These impurities exert powerful but variable effects on the properties of the raw rubber and the finished products made from it. No two shipments are exactly alike. The properties of raw Hevea rubber are not those of pure *cis*-polyisoprene, which in itself is highly sensitive to complex oxidation. Obviously, Hevea rubber is not a satisfactory object for fundamental research. The student should not be surprised that the huge literature on rubber is filled with confusing data and statements. It should be interpreted with caution.

1302. Man-made Raw Rubbers. Synthetic raw rubbers are produced by emulsion polymerization or other techniques described in Secs. 422 *ff*. A typical emulsion-polymerization batch is presented in Table 13-3 to

TABLE 13-3. TYPICAL EMULSION-POLYMERIZATION BATCH FOR BUTA S OR BUTA N

Material	Parts by wt
Butadiene.....	50-85
Styrene or acrylonitrile.....	50-15
Emulsifier (often soap).....	1-5
Buffer (often sodium acetate or phosphate).....	1-5
Polymerization catalyst (inorganic or organic peroxides, peracids, perborates, persulfates, etc.).....	0.1-1
Orientation catalyst (highly chlorinated aliphatics such as CCl ₄ , inorganic cyanides, organic sulfur compounds).....	0.1-1
Water.....	100-400

Polymerized at 35 to 60 C for 5 to 20 hr at 3 to 5 atm pressure (butadiene is a gas at room temperature and 1 atm pressure).

show the types of impurity that one may expect to find in the product. The important point is that synthetic products are manufactured under controlled conditions, and the amount and character of impurities are more constant and are more likely to be known.

MASTICATION AND MILLING

1303. The mechanical mastication of raw rubbers requires enormous power. Tremendous shearing stresses are set up in the mass. Unless cooling facilities are afforded, the rubber becomes very hot. Static charge is accumulated; if the milling is done in the dark, sparks may be observed. There is little question that very high temperatures are

attained at isolated points in the rubber, quite apart from its bulk temperature. The sparking may well lead to the formation of ozone, minute amounts of which will supply active radicals for peroxidation of olefinic structures (Sec. 1212).

When Hevea rubber is milled, it breaks down readily to a smooth, weak, puttylike mass. After mastication its solubility is greater and its solution viscosity lower. These effects increase with the time of milling (Fig. 13-1). Unquestionably, degradation takes place.

Very small but definite amounts of oxygen are absorbed by Hevea rubber when it is milled in air. However, when the operation is conducted in an inert gas, relatively little breakdown results and the milling process is very slow. Raw butyl rubber containing 1 per cent or less of the unsaturation of Hevea rubber undergoes relatively little breakdown. It was pointed out in Sec. 1212 that only a few hundredths of 1 per cent oxygen need react with Hevea rubber to reduce its molecular weight to half via oxidative degradation. These facts show conclusively that oxidative degradation, purely mechanical degradation, or both may occur during milling, depending on the chemical nature of the rubber and the milling conditions.

Owing to Diels-Alder and other side reactions (Sec. 430), raw synthetic buta rubbers always possess some primary-valence cross-links; *i.e.*, to a greater or lesser extent, they are "prevulcanized" before they reach the compounding equipment. Consequently, they are more difficult to break down than linear-polymeric Hevea rubber. This is of serious import in production.

The objectives in commercial milling are to break down the rubber and compound it as quickly as possible and to degrade it only as much as necessary for the intended application. This saves time and minimizes power cost. Lowering the average molecular weight of the binder beyond what is necessary is to be avoided, since, the greater the breakdown, the poorer the mechanical properties of the final product [Eq. (12-36), p. 544].

It is common practice, especially when mixes are loaded with large amounts of filler which reinforce the mass and raise its consistency, to add an external plasticizer (*e.g.*, pine tar), in the early stages of milling. The material is often called a *softener*. This permits the final desired plasticity to be reached in less time with less power and perhaps less

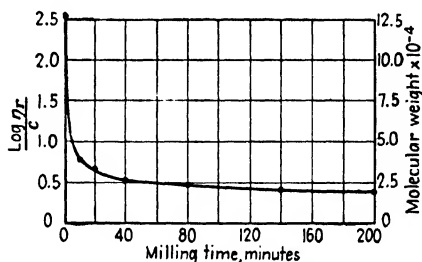


FIG. 13-1. Effect of milling time (at 95 F) on solution viscosity and molecular weight of raw Hevea rubber. [A. R. Kemp and W. G. Straits, *Ind. Eng. Chem.*, **36**, 707 (1944).]

degradation of the rubber itself. Since external plasticizer may bleed or leach out or too drastically modify the properties of the final product, the amount that may be added is limited.

In this regard, raw synthetic rubbers require so much softener that this led to the development of so-called *vulcanizable plasticizers*. A vulcanizable plasticizer is one that is eventually capable of becoming attached to the binder by primary valence bonds during vulcanization. Thus, it exerts its plasticizing action during milling and does not bleed or dissolve out of the finished vulcanizate. Unsaturated hydrocarbon oils and vegetable oils that are sulfur-reactive are often used for the purpose. Special phenol-aldehyde resins are also used; these are quasi-liquid at milling temperatures and become cross-linked at vulcanizing temperatures.

SULFUR VULCANIZATION

1304. At the current writing sulfur is still the most widely employed vulcanizing agent. It will vulcanize Hevea, butyl, buta S, and buta N rubbers. It does not vulcanize neoprene or thiokols, for which metallic oxides or even heat alone are effective.

1305. Soft and Hard Vulcanizates. If a sulfur-vulcanizable rubber is chemically reacted with relatively small amounts of sulfur, 0.5 to 5 parts per 100 of raw rubber,¹ the product is a soft, pliable, extensible *soft vulcanizate*. The remarkable improvements attending this process have been shown in Tables 12-1 and 12-2.² Some important properties that remain relatively unchanged are density, coefficients of expansion and compression, and electrical and thermal conductivities.

If the raw rubber is made to react chemically with large quantities of sulfur, 30 parts or more, a rigid, nonextensible *hard rubber*, or *ebonite*, results. This very useful product is relatively stable to heat, light, and air, requiring no antiaging compound since much of the unsaturation has been eliminated by reaction with the sulfur. Physically speaking, hard rubber is a plastic. Typical properties are listed in Table 13-4 (compare with Table 12-1).

¹ Rubber mixes are usually based on 100 parts of raw rubber. The relative amount of any compounding ingredient is quoted as "so-and-so many parts," meaning the parts by weight of this ingredient added per 100 parts by weight of raw rubber, as in Table 8-1, page 311. (See, however, Table 13-8, page 568.)

² Attention is again called to the fact that the tensile strengths of rubbers are normally reported as the breaking load divided by the *original* cross section. In a highly extensible material this value is radically different from that calculated on the basis of the actual cross section at break. Thus, for the soft vulcanizate of Table 12-1, the actual tensile stress at break is nearer 27,000 ($9 \times 3,000$) than 3,000 psi. In some of the figures and tables of this chapter this "true" tensile strength is listed.

TABLE 13-4. TYPICAL PROPERTIES OF A HARD RUBBER
(Sulfur-vulcanized Hevea)

Property	Value
Tensile strength, psi.....	10,000
Elongation at break, %.....	4
Permanent set.....	Small
Water absorption (315 days immersion), %.....	0.25
Swelling in solvents.....	Relatively slight
Tackiness.....	Negligible

It has been shown that sulfur vulcanization is attributable to cross-linkage, and it has been demonstrated quantitatively that the number of cross-links required to produce a good soft vulcanizate is small, for example, 1 cross-linked unit in no more than about 600 monomer units in the case of butyl rubber (Sec. 1223). The properties of soft vs. hard rubbers are in the main satisfactorily explained by postulating a small number of cross-links in the former and a large number in the latter.

Hard rubbers may be produced from Hevea, buta S, and buta N, but not from neoprene, thiokol, or butyl rubber.

1306. Vulcanization Coefficient vs. Physical Properties. It is common practice to use tensile properties as a yardstick for vulcanization. These are perhaps as good as any since they are easily measured important properties of the finished vulcanizate and can be correlated to molecular structure [Eqs. (12-36), page 544, and (12-41), page 550].

The *vulcanization coefficient* as used in this text is defined as the amount of sulfur that combines chemically with a rubber during vulcanization, expressed as parts by weight of sulfur per 100 parts of raw rubber.

Figure 13-2 shows tensile properties plotted against vulcanization coefficient for products obtained by curing a simple mix composed of 100 parts of raw rubber and 50 parts of sulfur (no accelerator) for different lengths of time. (This is not a commercial mix.) It will be seen that there are three regions. The first is a low vulcanization-coefficient region in which there is a great improvement in physical properties, until a maximum is reached. This is followed by a middle region of intermediate coefficient values in which there is just as noteworthy a drop in physical properties. Finally, there is a third region of high vulcanization-coefficient values in which there is again improvement in tensile strength.

In the first region (low vulcanization coefficients) the products are strong, highly extensible soft vulcanizates, and the first set of peaks represents *optimum cure* for these stocks. The middle region is called the region of "leathery" stocks. The products are semihard, semistiff, and lacking in strength, extensibility, and chemical stability. In the third region, where the vulcanization coefficients are high, the products

are typical hard rubbers, strong, rigid, and chemically stable, and the second peak of the tensile curves represents their optimum cure.

The successive changes in tensile strength in the three regions are more

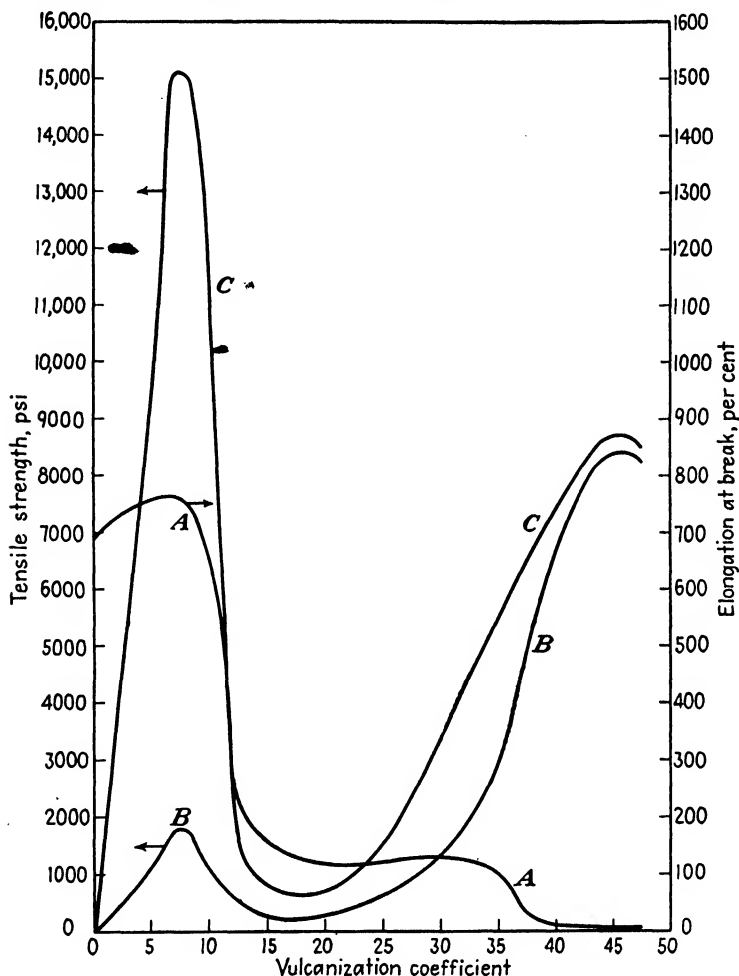


FIG. 13-2. Tensile properties as function of vulcanization coefficient for Hevea-rubber vulcanizate. (Unaccelerated mix of 100 parts rubber and 50 parts sulfur heated at 142 C for various times.) Curve A: elongation at break. Curve B: tensile strength (as ordinarily reported). Curve C: "true" tensile strength (on basis of actual cross section at break).

truly reflected by curve C, the plot of true tensile strength, than by curve B, which shows tensile strength as ordinarily reported. If it is assumed that soft vulcanizates contain very few cross-links or fix points and hard vulcanizates a large number, these apparently anomalous changes are at least partly explainable by the theory proposed in Sec. 909.

In commercial practice, modern soft vulcanizates have vulcanization coefficients of 4 or less (seldom higher than 3), while for hard rubbers the value is usually 30 or more. Stocks with intermediate coefficients are avoided for obvious reasons.

One might be led to believe that the vulcanization coefficient could be used as a quantitative measure of vulcanization, but this is not so. For instance, in simple rubber-sulfur mixes, the original sulfur concentration has a considerable effect on the tensile strength-vulcanization coefficient relationship. High concentrations of sulfur result in higher tensile strengths for a given coefficient in the soft-vulcanizate region. Furthermore, the introduction of vulcanization catalysts (accelerators) causes drastic changes, as shown in Fig. 13-3. Whereas a maximum tensile strength of 1,800 psi is attained at a vulcanization coefficient of 8 in the unaccelerated mix of Fig. 13-2, excellently cured soft vulcanizates with tensile strengths of 3,500 psi may be produced in accelerated mixes with coefficients as low as 0.5. In other words, vulcanizates that have reacted chemically with the same amount of sulfur may have radically different properties.

1307. Effects of Curing Temperature and Time. Attention will now be centered on soft vulcanizates. Working with a given mix of constant composition, the effects of curing temperature and time are found to be as follows:

1. The rate of vulcanization increases with temperature, the temperature coefficient determined either by change in physical properties or sulfur addition being about 2.5 per 10 C rise.

2. At any constant curing temperature the tensile strength first rises, reaches a maximum (optimum cure), and then falls again at a more or less rapid rate if the heating is continued. This is called *overcure*. In general, mixes which are heated at high temperatures or for long periods of time do not attain as high strengths as those which cure quickly or at low temperatures.

3. Changes in the curing temperature result in considerable differences not only in the optimum tensile strength but also in the shape of the curing curve (Fig. 13-4).

Working with mixes of varying composition cured at a constant temperature (Fig. 13-3), the following noteworthy facts emerge:

4. The more rapid the rate of sulfur addition during the very early stages of cure, the more rapid the initial rise in tensile strength.

5. In the early stages the ratio of sulfur atoms reacted to double bonds lost is not constant but varies from 1 to 2 or more from one mix to another.

6. The decline in tensile strength beyond the point of optimum cure occurs when the *rate* of sulfur addition decreases.

These behaviors coupled with the fact that the *total* amount of sulfur which reacts chemically with the rubber is not a measure of vulcanization prove that there are at least two reactions occurring between the sulfur and the rubber. Present knowledge does not permit their quantitative

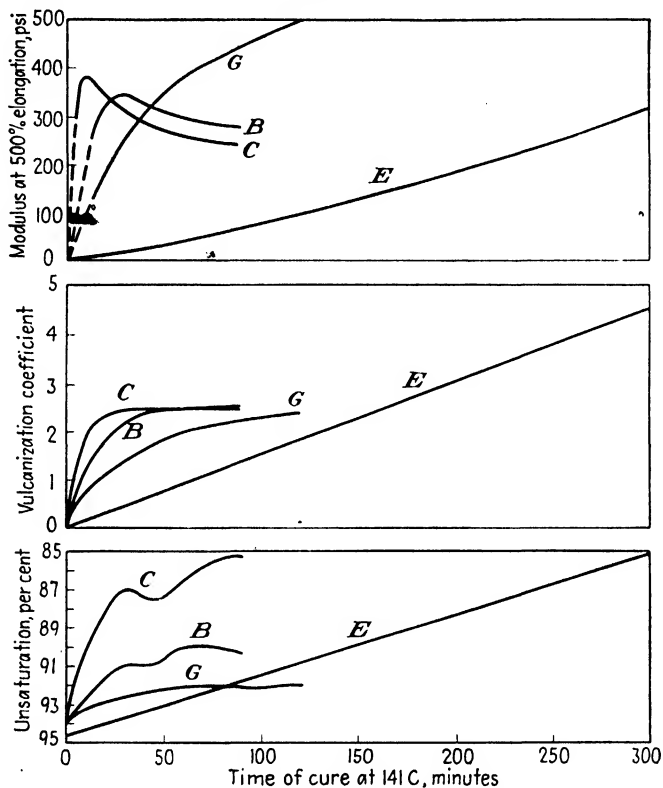


FIG. 13-3. Physical and chemical properties of Hevea-rubber vulcanizates as a function of time of cure.

Stock	B	C	E	G
Pale crepe	100	100	100	100
Sulfur	2.5	2.5	8	2.5
Zinc oxide	5.0	5.0	...	5.0
Stearic acid	0.5	0.5	...	0.5
Mercaptobenzothiazole	1.5
Zinc dimethyldithiocarbamate	...	0.5
Diphenylguanidine	1.0

[J. R. Brown and E. A. Häuser, *Ind. Eng. Chem.*, **30**, 1291 (1938); **31**, 1225 (1939).]

elucidation. They also indicate that degradation reactions, oxidative or otherwise, are occurring during cure.

Without attempting to disentangle the various reactions, it is obvious that the chemical changes accompanying vulcanization fall into two categories:

1. A building-up process, which enhances physical properties. From the evidence presented in Chap. 12 it is safe to state that this is the introduction of cross-links or metal-ionic bridges as fix points.

2. A tearing-down process, which damages the physical properties. This process may be ramified. First, cross-links formed during the early stages of cure may be ruptured in secondary reactions. Second, scission

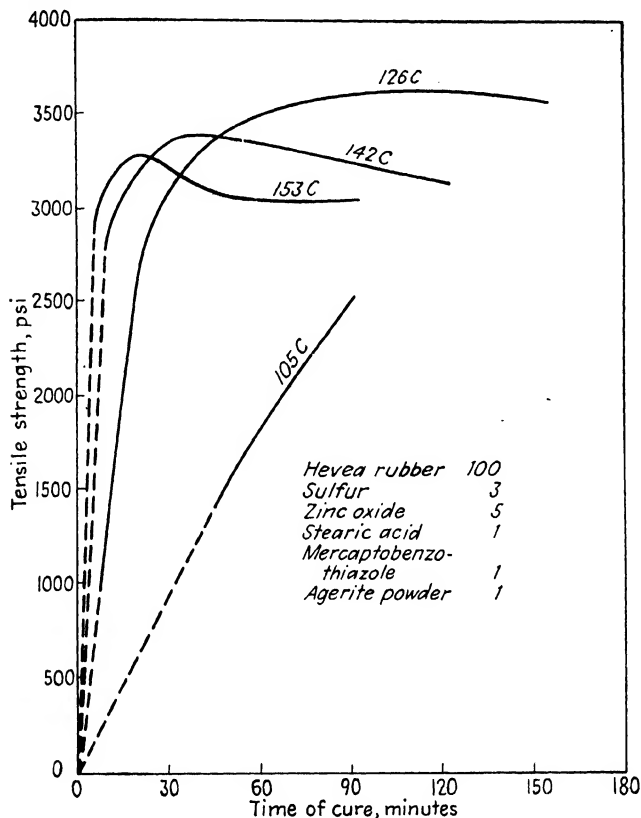


FIG. 13-4. Effect of temperature on rate of vulcanization and shape of curing curve. [Vanderbilt News, 3, No. 4 (1933).]

of the chain sections may take place. Since vulcanized Hevea rubber, especially when overcured, is notoriously susceptible to oxidative breakdown even at room temperature, part of the tearing-down process might well be thermally induced oxidative degradation. Badly overcured stocks are said to undergo "reversion." There is a notable loss in strength, and the product becomes soft and tacky and is particularly susceptible to further rapid deterioration on aging. These are all behaviors of an oxidatively degraded rubber. That the tearing-down process

cannot be attributed merely to an increase in vulcanization coefficient into the region of leathery stocks is evident from the fact that it takes place even when, and, indeed, especially when, heating is not accompanied by further sulfur addition.

It is obvious that any given mix may be undercured or overcured. The objective in commercial practice is to select curing conditions that yield the best physical properties that practical considerations will allow.

1308. Effects of Accelerators. A simple mixture of sulfur and raw rubber vulcanizes very slowly over a matter of 4 hr or more (Fig. 13-3). A large amount of sulfur must be added, a considerable part of which tends to remain unreacted, and a high vulcanization coefficient (about 6) is required to reach optimum cure. It was early discovered that mild improvement results when oxides of lead, zinc, calcium, or magnesium are incorporated into the mix. These compounds are known as *inorganic accelerators*.

Accordingly, until about 1900, soft rubber mixes required several hours to vulcanize, which meant slow, expensive production. The physical properties of the vulcanizates were relatively poor owing to extensive tearing-down action on the rubber. So much unreacted sulfur was present that some ultimately diffused to the surface of the finished goods, forming the unsightly grayish discoloration known as *bloom*. (About 1 per cent free sulfur is sufficient to produce bloom.) Finally, since relatively high vulcanization coefficients were required and since it is generally true that susceptibility to deterioration by aging increases with increase in the combined sulfur content, the service life of the finished goods was short.

The rubber industry was literally revolutionized by the discovery and introduction of modern synthetic organic accelerators. The principal commercial types are dithiocarbamates, thiuram sulfides, thiazoles, guanidines, and aldehydeamines. As shown in Table 13-5 they may be classified into three arbitrary groups in accordance with their relative efficacies in catalyzing vulcanization (of Hevea rubber).

It might be asked why ultraaccelerators are not used to the exclusion of all others. For one thing, they must be very carefully watched during milling and subsequent storage of the mix lest premature vulcanization take place, ruining the batch. This is called *scorching* and is of real concern in commercial practice. Also, in vulcanizing thick sections there is a tendency for outer surfaces to be overcured when ultraaccelerators are employed.

The spectacular improvements achievable with these accelerators are partly realized from Figs. 13-3 and 13-5 and Table 13-5. By reducing the time, temperature, or both required to cure the rubber, notable

savings are effected through more rapid molding cycles and lower fuel consumption. Equally important are the notable improvements in the finished products. The low total sulfur requirements eliminate bloom and greatly enhance the resistance to aging. Better mechanical properties result since the rubber molecules undergo less degradation during cure.

TABLE 13-5. ARBITRARY CLASSIFICATION OF ORGANIC ACCELERATORS
(Behavior in vulcanization of Hevea rubber)

Type	Amount commonly added to mix, parts per 100 parts of raw rubber	Amount of sulfur commonly used, parts per 100 parts of raw rubber	Conditions under which cure is attainable	Examples
Ultra-rapid.	0.25-0.5	0.5-2	A few minutes at temperatures as low as 100 C	Tetramethylthiuram disulfide. Zinc diethyl-dithiocarbamate
Semi-ultra.	0.5-1.5	2-3	30 min at 100 to 140 C	Mercaptobenzothiazole
Rapid . . .	1.0-1.5	2-4	Still longer times at temperatures around 140 C	Diphenylguanidine

One other benefit of major technological importance accrues from modern accelerators. Consider two curing curves, *A* and *B*, in Fig. 13-6. *A* represents great advantages. It means that the mix may be heated for relatively long periods of time without suffering much damage or overcure. Rubbers are exceptionally poor conductors of heat. Being almost devoid of polarity, they are likewise very difficult to heat electronically. For these reasons, only with an accelerator having a table-top cure can heavy sections be vulcanized without overcure of the surface or undercure of the interior. Again, in making continuous members such as heavy, rubber-covered conveyer belting, the piece is introduced into the vulcanizing equipment in successive sections. This means that points along the belting are, in effect, vulcanized twice. The table-top effect avoids bad overcuring at these points.

It is seen from Fig. 13-4 that for any given accelerator the flatness of the curing curve is dependent on the temperature of vulcanization. Since modern accelerators permit rapid cure at relatively low temperatures, they tend to make table-top cures possible. A more potent method for inducing this type of cure is to use a high ratio of accelerator to sulfur.

Notably flat curing curves may be attained by this technique, and the finished vulcanizates exhibit outstanding resistance to heat and aging.

Once again the reader is warned to bear in mind that the efficacy of any given accelerator may vary enormously according to the type of rubber with which it is used. Thus, tetramethylthiuram disulfide, an

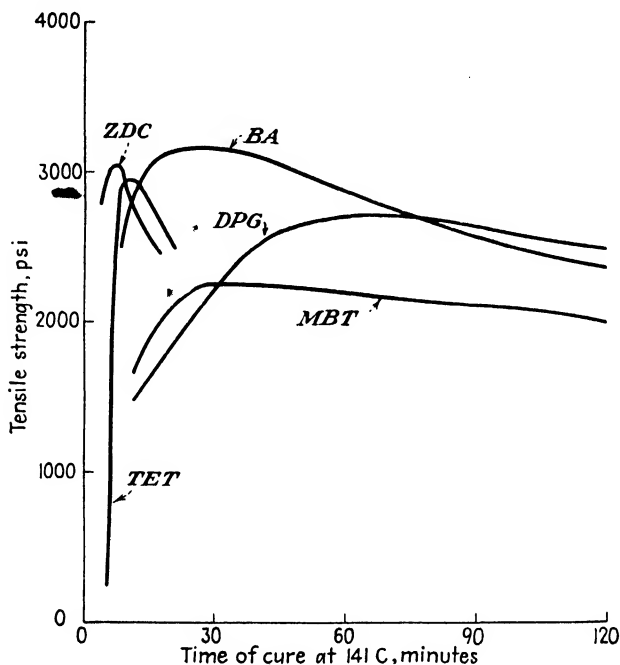


Fig. 13-5. Action of various organic accelerators.

Stock	DPG	MBT	BA	TET	ZDC
Raw Hevea rubber	100	100	100	100	100
Zinc oxide	10	10	10	10	10
Stearic acid	2.0	2.0	2.0	2.0	2.0
Sulfur	3.0	2.5	2.5	2.0	2.0
Diphenylguanidine	1.0				
Mercaptobenzothiazole		0.625			
Butyraldehyde aniline			0.5		
Tetraethylthiuram disulfide				0.375	
Zinc diethyldithiocarbamate					0.375

[M. Jones, *Trans. Inst. Rubber Ind.*, **11**, 37 (1935-36).]

ultraaccelerator for Hevea, is an accelerator retarder for neoprene. Similar affects are found with other compounding ingredients.

1309. Accelerator Activators. The statement that organic accelerators are responsible for the benefits described previously is a half truth. They do not exert startling effects unless proper activators are also present. It is now generally recognized that most efficient sulfur vulcanization requires the presence of all four of the following: sulfur,

organic accelerator, metallic oxide (most often zinc oxide), and rubber-soluble metallic soap (usually zinc stearate or laurate). The last two items act as accelerator activators (promoters). The soap is often formed during cure by the interaction of metallic oxide with added fatty acid. Just how necessary the activator may be will be appreciated from the data of Table 13-6.

TABLE 13-6. EFFECT OF ACTIVATOR ON VULCANIZATION

Time of cure, min	Tensile strength, psi	
	No zinc oxide	5 parts zinc oxide
15	100	2,300
30	400	2,900
60	1,050	2,900
90	1,300	2,900

GARVEY, B. S., JR., and G. THOMPSON, *Ind. Eng. Chem.*, **25**, 1292 (1933).

Base mix: Pale crepe 100; sulfur 3; mercaptobenzothiazole 0.5.

Vulcanization temperature: 142 C.

The following points should now be considered in connection with the vulcanization of mixes of the above-mentioned composition.

1. Rate of cure is greatly influenced by pH. In general, acids that reduce the pH below 3 retard vulcanization to the point where satisfactory cure can scarcely be attained.

At higher pH's the rate of cure increases, but there are indications that if it is too high (above 8), reversion is so rapid that satisfactory vulcanization is not obtainable.

2. Salts and oxides of bivalent metals such as lead, calcium, magnesium, and zinc markedly increase the rate of cure. Their solubility in the rubber is important. In general, soluble compounds such as zinc stearate lead to rapid cure whereas insoluble ones like zinc sulfide result in slow cure.

3. X-ray diffraction studies indicate strongly that organic accelerator and divalent metallic ions from activators combine chemically with the rubber molecules during vulcanization. Other experiments can be cited which indicate that the introduction of divalent metallic ions into a vulcanizate containing no divalent metal increases the tensile modulus,

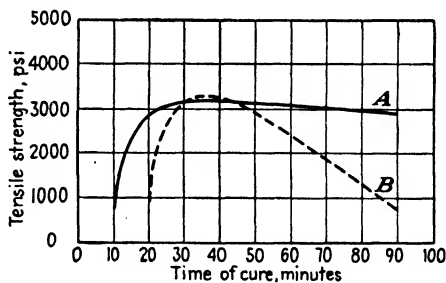
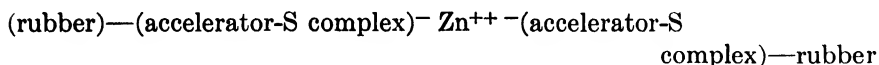


FIG. 13-6. Curing curves in rubber vulcanization. Curve A: desirable table-top, or plateau, cure. Curve B: undesirable type of cure. [*Vanderbilt News*, **4**, No. 6 (1934).]

while their removal decreases the modulus. A good case can thus be made for the formation during vulcanization of ionic bridges of the type



From the above discussion it follows that so-called accelerator activators such as zinc salts are more than mere promoters and that besides catalyzing the reactions between rubber, sulfur, and organic accelerator, they may contribute substantially to the physical properties of vulcanizates by supplying bivalent metallic ions which participate in the formation of strong, secondary-valence salt bridges. It may eventually turn out that this kind of bridging rather than primary-valence bonding via sulfur is mainly responsible for the physical changes called vulcanization in systems of this kind.

Although lead, calcium, and magnesium activators are more or less effective, zinc compounds are the most generally used. They are effective with all common accelerators, are readily soluble in rubber, and do not discolor or darken the finished product. At the current writing almost all sulfur-vulcanized rubber products are based on the composition range shown in Table 13-7. If nothing else is added, the cured product is a

TABLE 13-7. COMPOSITION OF HEVEA PURE-GUM VULCANIZATES
(Sulfur-vulcanized)

Material	Parts by wt
Raw-rubber hydrocarbon.....	100
Sulfur.....	0.25-1.5
Accelerator.....	0.25-1.5
Activators:	
Zinc oxide.....	1-10
Stearic acid or zinc laurate.....	1-5
Aging retarder.....	0-1.5

A loaded stock is made by incorporating filler (and often softener) in the pure-gum mix. Any additional ingredients may be regarded as special-purpose or incidental items.

typical pure-gum vulcanizate. A loaded stock is made merely by incorporating filler to the pure-gum recipe. As a rule, "softener" is also added to a loaded stock as a milling aid. Coloring agents and special-purpose compounding ingredients may also be incorporated but are of secondary importance.

It has been found that mixed accelerators often are more active than either alone. A common example is the combination of a guanidine (basic) and a thiazole (acidic). This sort of activation usually requires that standard activators, *viz.*, zinc oxide and stearic acid, be present as usual.

LOADING

1310. Table 13-8 shows effects on the mechanical properties of cured vulcanizates produced by incorporating a fixed volume of various powdered solids into a Hevea-rubber base mix. The properties of the unloaded pure-gum vulcanizate are included for comparison.

Reinforcement is broadly defined as the increase in the service life of a tire tread or similar item resulting from the improvement of mechanical properties brought about by the incorporation of a powdered solid filler. A *reinforcing filler* is one that increases tensile strength, abrasion resistance, tear resistance, or any combination of the three. Modern industry could no longer function properly without reinforced rubber.

Under the above definition, inspection of Table 13-8 reveals that some fillers like channel black are strongly reinforcing in all three aspects; others like the fine thermal black and magnesium carbonate reinforce some properties while weakening others; still others such as gilder's whiting are completely nonreinforcing, actually weakening the vulcanizate in all three respects. These latter are very definitely *inert fillers*. Further inspection of Table 13-8 reveals that no matter whether a filler is reinforcing or inert its presence results in an increased consistency, or "stiffness," as measured by the 400 per cent modulus, for reasons advanced in Sec. 1211. This increase in consistency varies radically from one filler to the next.

1311. Factors Affecting Reinforcement by Loading Agents. In accordance with the generalizations of Sec. 935, the reinforcing action of a loading agent depends upon several factors, among which are (1) the nature of the binder; (2) the nature of the loading agent, with especial regard to its chemical composition, surface condition, particle size, and particle structure; and (3) the relative amounts of binder and loading agent.

1312. The Nature of the Binder. From Table 12-2 it is evident that carbon black, a powerful tensile reinforcing agent for Hevea, buta S, buta N, and Thiokol, does not enhance the ultimate tensile strength of neoprene or butyl rubber. (Abrasion and tear reinforcement occur for all.) There is a logical explanation for this behavior. It has been shown in Sec. 1227 that high ultimate tensile strength in a vulcanizate depends largely on the ability to crystallize at high elongations. A reinforcing filler introduces a large number of relatively weak surface-force fix points, thus tending to stiffen the structure. At the same time, it takes up space and may interfere with close packing and crystallization of the polymer chain sections. Whether the end result will be an increase or decrease in tensile strength depends upon which of these conflicting effects predominates.

TABLE 13-8. EFFECTS OF LOADING AGENTS ON MECHANICAL PROPERTIES OF A VULCANIZATE*†

Loading agent		Tensile strength, psi	Elongation at break, %	"True"‡ tensile strength, psi	"Stiffness," § (400% modulus), psi	Abrasion resistance	Tear ¶ resistance, lb/in. thickness
Type	Parts by wt/100 parts raw rubber						
Channel black.....	41.4	4,690	615	33,600	2,260	256	759
Fine thermal black (P-33).....	41.4	4,250	690	33,600	830	132	496
Magnesium carbonate.....	51.3	4,220	620	30,400	1,450	117	147
Zinc oxide.....	130.0	3,970	615	28,400	1,310	181	320
Dixie clay.....	59.8	3,770	520	23,400	2,120	135	143
Kalite No. 1 (treated whiting).....	61.0	3,510	620	25,300	820	115	283
Blanc fixe.....	96.6	3,460	570	23,200	1,290	131	272
Titanium oxide.....	90.6	3,450	590	23,800	1,550	188	332
Kalite No. 3 (treated whiting).....	58.9	3,430	650	25,700	710	107	282
Medium thermal black (Thermax).....	41.4	3,400	640	25,200	1,050	127	291
Lithopone.....	96.6	3,370	570	22,600	1,290	147	251
Pure-gum vulcanizate.....	(Unloaded)	3,350	675	26,500	405	186	236
Gilder's whiting.....	62.3	2,860	580	19,400	890	89	122
Limestone whiting.....	62.3	2,650	600	18,600	720	78	108
Talc.....	59.8	2,480	590	17,100	670	67	89

* Based on data in *Vanderbilt News*, 3, No. 3 (1933).

† Base mix: Raw (Hveva) rubber 100 parts, zinc oxide 5, stearic acid 1, Agerite powder 1, sulfur 0.5, selenium 0.5, mercaptobenzothiazole 0.5, tetramethylthiuram disulfide 0.5. Loading agent: 23 volumes per 100 volumes raw rubber. All mixes vulcanized at 135°C (275°F) to optimum cure (maximum tensile strength).

‡ Calculated to actual cross section at break.

§ Tensile stress at 400 per cent elongation.

|| Reciprocal of abrasion loss, Kelly machine test.

¶ Crescent test.

1313. The Nature of the Loading Agent. Table 13-8 shows that chemical constitution is one determinant of reinforcement. For example, talc, no matter how finely ground, does not effectively reinforce Hevea rubber. The significance of surface condition is illustrated by the Kalites, gilder's whiting, and limestone whiting listed in the same table. The Kalites are coated whittings containing a few per cent of stearic acid. They reinforce, whereas the untreated whittings do not.

Particle size is a dominant factor. In general, the reinforcing action increases as the particle size of a filler decreases. The channel, fine thermal, and medium thermal blacks of Table 13-8 are carbons of increasing size. Particle structure is also of importance, as recent studies have shown.

The above factors are the very ones expected to be important if surface forces acting between the binder and filler account for reinforcement.

1314. The Relative Amounts of Binder and Filler. The effect of this factor is brought out in Fig. 13-7, where it is shown that for a given binder-filler combination, as the amount of filler is increased, tensile reinforcement first rises to a maximum and then drops. From the compounder's standpoint, a broad maximum is more advantageous than a sharp peak since it permits greater latitude in compounding.

1315. Carbons. By far the most important loading agents for rubber are the various colloidal forms of carbon. Indeed, if reinforcement of all three properties, tensile strength, abrasion resistance, and tear resistance, is required, colloidal carbons are the only inexpensive materials available that will fill the requirement.

The electron microscope makes possible the accurate determination of the sizes and shapes of these particles. They are spheroidal and exceed all other commercial loading agents in fineness, ranging from 90 A for

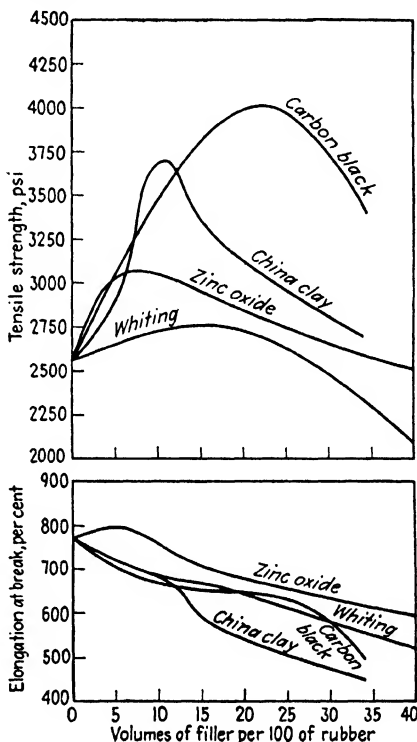


FIG. 13-7. Effects of loading agents on tensile properties of a Hevea-rubber vulcanizate. [H. Barron and F. H. Cotton, *Trans. Inst. Rubber Ind.*, 7, 209 (1931-32).]

extremely fine channel blacks to 3,000 Å for relatively coarse thermal blacks (Table 13-9). The electron microscope also reveals that in some

TABLE 13-9. PROPERTIES OF COLLOIDAL REINFORCING CARBON BLACKS

Designation	Particle size (diameter), Å	Structure index*	pH	Volatile matter, %	Tensile strength of Hevea vulcanizate containing 50 parts of the black, psi	Resistivity of the dry black compressed at 150 psi, ohm-cm
Highest color	90	100	2.8	19.0	33.0
Medium color	180	100	3.5	8.5	6.4
Conductive channel	210	120	4.2			
Hard processing channel	250	100	4.0	4,400	
Medium processing channel	270	100	4.5	4,300	
Easy processing channel	290	100	5.0			
Conductive furnace	360	100	10.0	0.6	1.6
Fine furnace	360	100	10.0	0.3	4,200	4.3
Acetylene	420	300	8.0	0.3	3,300	0.44
High-modulus furnace	500	160	10.0			
Semireinforcing furnace	800	100	9.0	0.2	3,400	4.3
Fine thermal	850	60	8.0	3,700	
Lampblack	1,000	200	4.0	3.0	3,200	5.6
Medium thermal	3,000	60	7.0	0.8	3,100	150

Based on data of SWEITZER, C. W., and W. C. GOODRICH, *Rubber Age* (N.Y.), **55**, 469 (1944).

* Calculated as percentage of normal oil absorption (see reference).

blacks the carbon spheroids are practically separate (low "structure index"), whereas in others they are joined to one another in continuous dendritic networks (high structure index) which persist even after drastic milling. These structures are shown schematically in Fig. 13-8. It has also been discovered that carbon-black particles vary in pH from 2.5 to 11 owing to the relative presence or absence of acidic and other oxygenated and hydrogenated structures enveloping the surface.

It is now possible to evaluate a black and predict many of its behaviors in terms of the three fundamental properties, particle size, structure index, and pH. In general, as particle size decreases, tensile modulus, ultimate tensile strength, hardness, toughness, abrasion and tear resistance increase, while rebound and ease of processing decrease. However, structure imposes its own effects. For example, acetylene black, with its unusually high structure index, is difficult to disperse and yields vulcanizates with abnormally high tensile modulus and hardness and abnormally low toughness, electrical resistivity, and ultimate tensile strength (marked interference with alignment of rubber molecules at

high elongation). The pH affects electrical properties and is especially interesting for its influence on curing rate. For example, acidic blacks retard vulcanization with diphenylguanidine and other alkaline accelerators, whereas alkaline blacks may increase the rate of cure.

1316. Choice of Reinforcing Carbon. For heavy-duty rubber it is essential to reinforce with carbon black. Tire-tread stocks normally contain 40 to 60 parts. Only in this way can adequate abrasion and tear resistance be imparted. But reinforcement with carbon black increases the consistency of the rubber and interferes with prompt disalignment of the rubber molecules when tension is released. The hysteresis loss under cyclic stress (such as a tire is subjected to in road use) is increased. Hence reinforcement decreases snap and resilience and increases the temperature rise accompanying cyclic stress. If this *heat build-up* is excessive, tensile strength, tear resistance, and abrasion resistance are lowered, oxidative deterioration and heat embrittlement are accelerated, and sudden failure in the form of a blowout may take place. Thus the use of reinforcing filler represents a compromise.

For tire tread, a strongly reinforcing carbon like channel black (Table 13-8) is used when possible in spite of the high stiffness it imparts. On the other hand, if an article is of such character that it must be soft and pliable and tensile and tear reinforcement are of greater consequence than abrasion resistance, a thermal black such as the fine thermal of Table 13-8 might be used (*e.g.*, for a black inner tube). If ease of compounding is a major factor, a coarse black is most suitable.

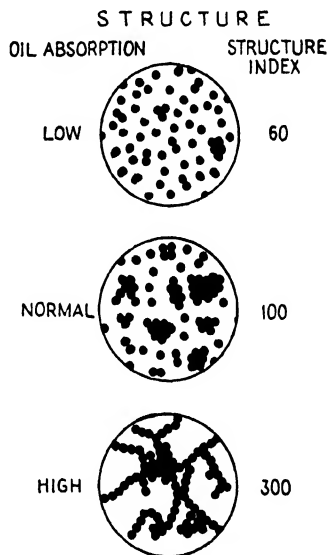


FIG. 13-8. Schematic representation of structure in several carbon blacks. [C. W. Sweitzer and W. C. Goodrich, *Rubber Age* (N.Y.), **55**, 469 (1944).]

RESISTANCE TO HEAT, LIGHT, AND OXIDATION

1317. Some rubbers are inherently more stable chemically than others. Thus, as one might expect, butyl rubber, which is practically saturated, and neoprene, which is chlorinated, are generally more resistant to attack by heat, light, and oxidants than Hevea, buta S, and buta N (see Table 12-3, page 514).

The physical deteriorative changes that occur in rubber on exposure

to heat, light, and air are collectively known as *aging*, and it has been shown by many different experiments that aging must be associated with a chemical reaction involving oxygen. Unless proper preventive measures are taken, the service life of a soft rubber vulcanizate is normally so short as to preclude it from many applications. As previously indicated in Sec. 1212, aging can follow different paths. The one effect, by which the rubber grows soft and tacky, involves degradation; the other, by which the rubber turns hard and brittle, appears to be an undesirable vulcanization. It may be caused by oxygen (or ozone) or by a slow, progressive sulfur vulcanization called *after-vulcanization*.

It has been found that the conditions under which the vulcanizate is used influence both the rate and the path of deterioration (Secs. 1330 ff.). High temperatures are generally detrimental. A Hevea-rubber vulcanizate kept under slight tension (5 to 20 per cent elongation) deteriorates far more rapidly than the same rubber at rest or at high elongations. Since cyclic stress causes heat build-up and subjects parts of the tread to bending, a tire tends to fail at the wall. For similar reasons, that portion of a rubber tube which is stretched over a nozzle may harden and crack rapidly. Diene rubbers are also attacked by short-wave-length light, which causes hardening and cracking. The problem of sun checking still has not been completely solved.

Manufacturing technique also plays its part. Overcuring, long curing in general, and high vulcanization coefficients induce rapid aging.

Second only to the development of organic accelerators, the discovery of modern antiaging compounds represents the most significant advance in rubber compounding since Goodyear's time. Aromatic amines of various types are particularly effective *aging retarders*. Different compounds exert specific action against different kinds of deterioration. Most diene rubber vulcanizates now contain phenyl- α -naphthylamine and phenyl- β -naphthylamine. Organic accelerators permit smaller vulcanization coefficients and faster cures. High accelerator-sulfur ratios induce table-top cure. In all these respects modern accelerators may contribute to greatly improved resistance to aging and deterioration. Finally, certain goods, especially those which are to be subjected to cyclic stress under drastic conditions, are deliberately left somewhat on the undercured side. By applying these several agents and techniques rubber vulcanizates with vastly improved resistance to deterioration may now be produced. Rubber articles that exhibit practically no aging after 5 to 10 years under room conditions are common.

Air-oven and oxygen-bomb tests at elevated temperatures are often conducted in the laboratory to accelerate the aging of specimens with the object of evaluating and predicting their behavior in service. The results

of these tests must be interpreted with caution, for reasons discussed in Sec. 1333.

STATIC MECHANICAL PROPERTIES

1318. Rheologically, rubber is viscoelastic (Fig. 7-7, page 266). Its engineering value lies in its uniquely enormous reversible extensibility and energy-absorbing capacity. Only a captive liquid (Sec. 516) could combine such characteristics. The mechanical evaluation of a rubber thus resolves itself into a twofold determination of its elasticity and its consistency. Furthermore, the merit of a rubber article for any intended mechanical application will depend on how judiciously these fundamental properties have been combined.

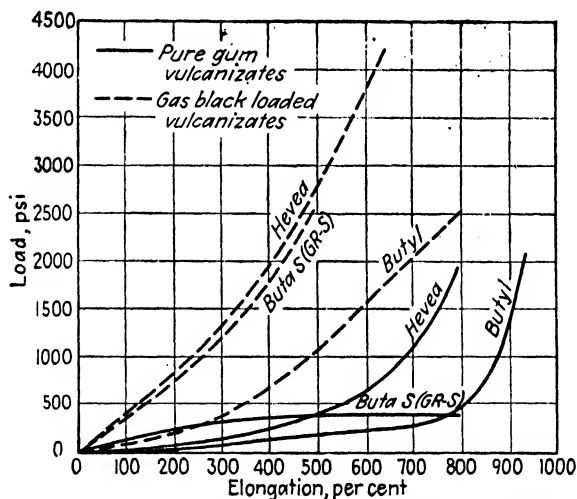


FIG. 13-9. Load-elongation curves of rubber vulcanizates.

1319. Static Tensile Properties. Various static properties of some important rubber products are listed in Appendix D. From prior discussion, the reader should be able to understand and predict along general lines the mechanical properties of rubbers compared with those of other classes of materials. For example, rates of creep and relaxation are high. Owing to the unusual reversible extensibility, toughness and resilience are outstanding (Table 9-17, page 415).

The tensile load-elongation curves of pure-gum vulcanizates differ radically in form and position depending upon molecular structure, polarity, and crystallization, *i.e.*, at what elongation crystallization starts and to what extent it takes place (Fig. 13-9). Buta S and buta N vulcanizates, owing to poor molecular symmetry, do not crystallize even at high elongation (Fig. 5-18). Even though the load-elongation curve of buta

S starts with a relatively steep slope, the tensile stress never attains the high value attributable to the self-reinforcing effect of crystallization so prominent in butyl and Hevea vulcanizates. While it is stiffer than Hevea rubber at low elongations, it is not so stiff at high elongations.

Figure 13-9 illustrates the enormous differences in the effect of reinforcing black on individual polymers. Carbon black does not improve the *ultimate* tensile strength of butyl rubber or neoprene vulcanizates. The interference with crystallization at high elongations overbalances the

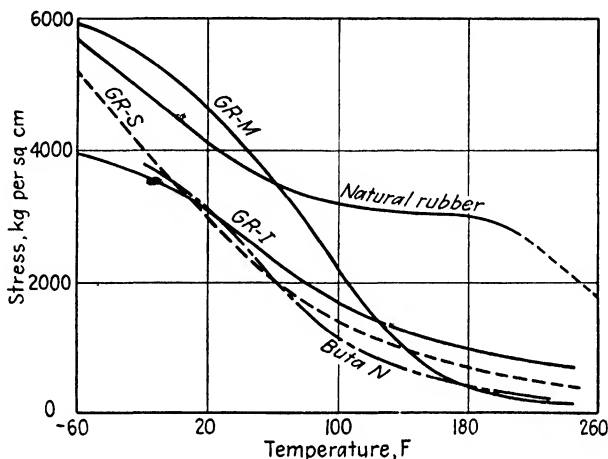


FIG. 13-10. Tensile strength as a function of temperature for various vulcanizates. [J. D. Morron, et al., *India Rubber World*, **110**, 521 (1944).]

reinforcing action of surface-force fix points. However, at low elongations, before crystallization is appreciable, the latter action predominates and the tensile moduli of the loaded stocks are higher than those of the gum vulcanizates.

The effects of temperature are of considerable interest since in modern technology the need for excellent low-temperature and high-temperature performance in elastomers grows continually more pressing. Figure 13-10 shows tensile strength as a function of temperature. It will be noted that Hevea rubber is in general less sensitive to temperature than synthetic elastomers, particularly near room temperature and in the range of most ordinary applications.

1320. Effects of Mechanical Conditioning. The reader should carefully review Secs. 710, 723–726, and 925–929.

Figure 13-11 shows what happens when a specimen of raw rubber that has been at rest for a long period of time is put through two successive “static” tensile-stress cycles. In the first cycle the original resistance to extension is relatively great, but considerable flow occurs, and the first

hysteresis loop and the set are enormous. (Since the second cycle was not started immediately, a small but definite retarded recovery shows in the diagram.) During the second cycle the resistance to extension is far less, as are energy absorption, hysteresis, and the amount of set. The important points to note are that (1) the rubber undergoes to a tremendous degree the process of mechanical conditioning and (2) to a very much greater extent than in other solids the mechanical properties, such as tensile strength, energy absorption, hysteresis, and set, depend upon the previous history of the specimen.

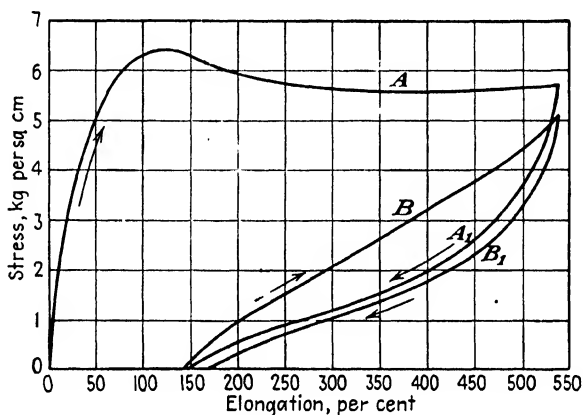


FIG. 13-11. Hysteresis loops for raw Hevea rubber. Extension rate = 2.85 per cent per sec. Curve AA_1 : first cycle of loading and unloading. Curve BB_1 : second cycle. [L. Hock and S. Bostrom, *Kautschuk*, **2**, 130 (1926).]

Vulcanization introduces fix points. This greatly emphasizes the elastic characteristics. Figure 13-12 shows the stress-strain cycle for a Hevea rubber before and after vulcanization. For the vulcanizate, tensile resistance has improved markedly, and set has been to all intents eliminated. The resilient energy is much greater, but the hysteresis loop is much smaller, which means less heat build-up during a stress cycle. It also means that the specific damping capacity has decreased, but this is no great disadvantage since it is still enormously greater than that of other structural materials. Briefly, whereas raw rubber is unfit for structural applications, vulcanized rubber, owing to its enhanced elasticity, is a stress-resisting material of unusual and valuable character.

Even vulcanized rubber undergoes extensive mechanical conditioning. A tensile specimen of Hevea tread stock was stretched to 400 per cent elongation and allowed to return to zero stress 10 successive times. Its tensile curve was then promptly determined. Figure 13-13 compares the curve of this specimen with that of an original, unflexed specimen. Notice that in this instance both the position and the shape of the curve

have undergone considerable change. It was found that after 10 cycles no appreciable further mechanical conditioning occurred.

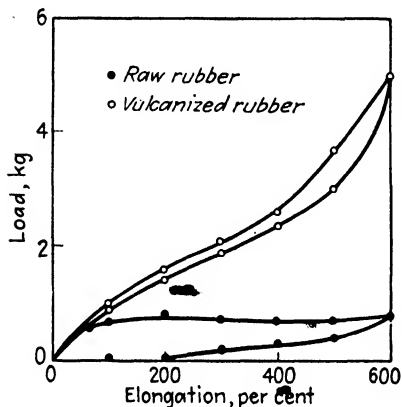


FIG. 13-12. Stress-strain cycles of a Hevea-rubber sample before and after vulcanization. [L. Hock and S. Bostrom, *Kautschuk*, **2**, 130 (1926).]

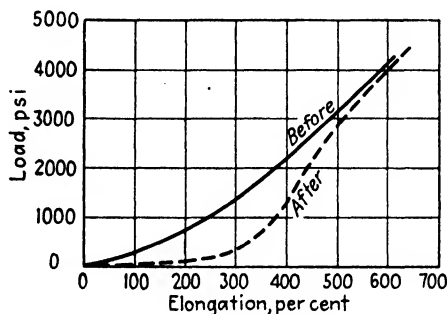


FIG. 13-13. Stress-strain curve of a Hevea-rubber vulcanizate before and after 10 stretchings to 400 per cent elongation. [H. A. Braendle and W. B. Wiegand, *India Rubber World*, **110**, 178 (1944).]

Rubbers exhibit considerable differences in hysteresis behavior. Thus the following results are obtained with Hevea and buta S (GR-S) tire-tread stocks under slow ("static") extension and contraction (Fig. 13-14).

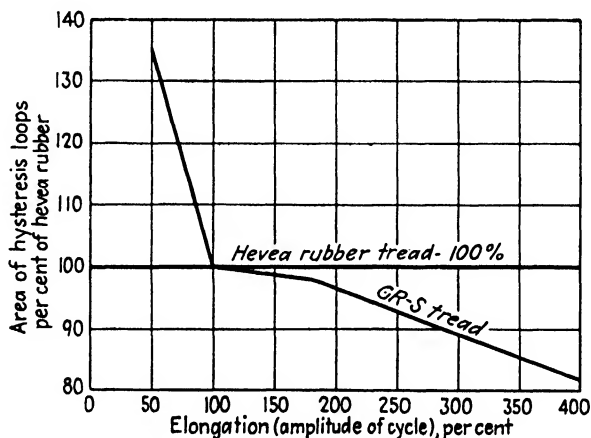


FIG. 13-14. Effect of elongation on "static" hysteresis loops of two vulcanizates. [W. B. Wiegand and H. A. Braendle, *Ind. Eng. Chem.*, **36**, 699 (1944).]

At 50 per cent elongation, buta S exhibits 35 per cent more hysteresis than Hevea; at 100 per cent elongation, about the same; at 400 per cent elongation, 20 per cent less than Hevea.

In Fig. 13-14 the two rubbers are compared by means of equal-

amplitude loops. If buta S is similarly compared with Hevea rubber under almost static conditions but stretching to equal *stress* rather than equal amplitude, it is found that Hevea rubber stretches much farther and shows greater energy absorption but also more hysteresis. Again, different *relative* amounts of hysteresis are found at different maximum stresses. Several important points are illustrated by these data.

1. The static stress-strain curve and hysteresis loop of an unconditioned rubber specimen are radically different from those of one that has been conditioned by cyclic stress.

2. The specific damping capacity, $D/(D + R)$ of Fig. 7-13, varies with the amplitude (maximum strain) of the cycle. Also, the relative amounts of hysteresis exhibited by two different rubbers varies depending on the amplitude of the cycle.

3. Specific damping capacity varies with the maximum stress of the cycle; and not only do the *relative* amounts of hysteresis of two different rubbers vary with the maximum strain, but this relative relationship is different from that existing when they are compared on the basis of equal amplitude.

To the above points one should add a fourth, that the damping properties of a material vary with the frequency of the cyclic stress.

Working with a tensile-testing machine, one investigator obtained loops which indicated that the hysteresis of Hevea tire tread was about six times greater than that of buta-S tread. It was thought that the heat build-up would be much less in buta-S tires. On the contrary, road tests proved it to be greater. This misleading result is directly attributable to the fact that the frequencies, amplitudes, and maximum stresses of the cycles set up in an automobile tire on the road are radically different from those used in the test method. If damping capacity and heat build-up in service are to be predicted with any degree of accuracy, the test conditions must closely approximate performance conditions.

DYNAMIC PROPERTIES

1321. Dynamic Relationships. A number of testing methods have been developed to measure rubbers under dynamic conditions. One type of machine sets up forced vibrations in the specimen. The frequencies and amplitudes of these vibrations are of the order that might be set up in a tire during road service. The dynamic modulus of elasticity E_d and the "viscous" resistance to deformation can be calculated from the properties of the system at resonance by using appropriate vibration equations. For want of a better name, this viscosity under cyclic stress η_A is called the *internal friction*. Since the two fundamental characteristics of the viscoelastic material, *viz.*, dynamic modulus of elasticity and

"coefficient of viscosity," are thus measurable, properties such as dynamic resilience, damping, and relative heat generation can be calculated from vibration equations.

The *dynamic resilience* is defined by Gehman and coworkers as the percentage of the vibrational energy that persists in the second of two successive *free* (not forced) vibrations. It depends on the fundamental constants of the rubber as follows:

$$R = 100\% e^{-4\pi^2 f \eta_A / E_d} \quad (13-1)$$

where f is the frequency in cycles per second and R the dynamic resilience in per cent. The per cent damping is then simply $100 - R$.

From vibration theory it can be shown that the *relative rates of heat generation* in different rubber compounds under different conditions of cyclic deformation should be approximately as follows: For constant driving force F applied to the rubbers,

$$H_F \propto \frac{(100 - R)F^2}{E_d} \quad (13-2)$$

In the case of *constant amplitude* x of the forced vibrations applied to the rubbers,

$$H_x \propto (100 - R)E_d x^2 \quad (13-3)$$

If the fundamental properties E_d and η_A are measured, R may be calculated from Eq. (13-1) and relative rates of heat generation determined from Eqs. (13-2) and (13-3).

1322. The Nature of the Internal Friction. It has been demonstrated that the internal friction η_A has the dimensions and characteristics in many respects similar to those of η , the viscosity of a liquid. The dependence of the latter on temperature is expressed by the usual exponential function

$$\eta = B e^{U/RT} \quad (13-4a)$$

$$\ln \eta = \ln B + \frac{U}{RT} \quad (13-4b)$$

For a rubber, if $\ln \eta_A$ is plotted against $1/T$, the points fall on straight lines intersecting at a break. The activation energy required for flow changes at the break point. Data for three rubbers are shown in Fig. 13-15. The break in each case probably represents a phase change. Thus, for Hevea rubber it falls at the temperature of first-order transition from the crystalline to the truly rubbery stable amorphous form (Fig. 5-20). It is highly significant that this transition does not take place in the synthetic rubbers until the temperature is well above room tempera-

ture. Theoretically, this might well mean that, for the latter at room temperature, the amorphous state is not the stable state.

1323. Relation between Dynamic and Static Modulus. For metals, fibers, and plastics the dynamic modulus is lower than the static modulus of elasticity. In rubbers it is higher (Fig. 13-20), at least in the regions of low elongation before crystallization occurs. Evidently, in the rubber

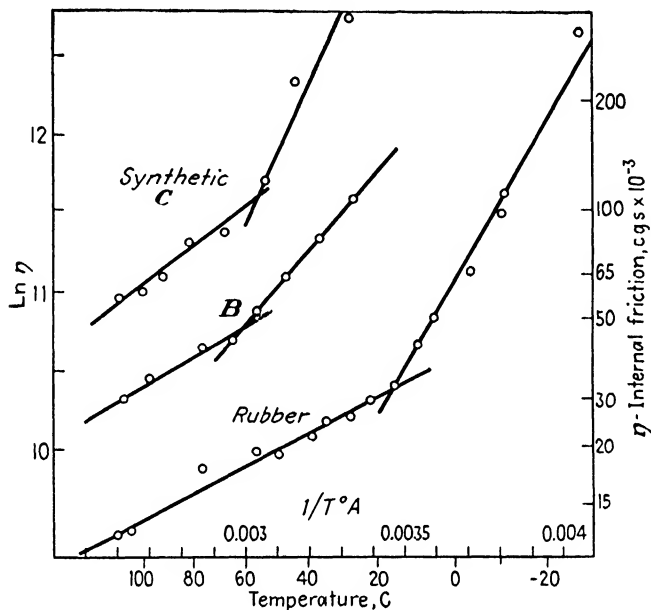


FIG. 13-15. Internal friction as function of temperature for three tread stocks. See Table 13-10 for identification of rubbers. [R. B. Stambaugh, *Ind. Eng. Chem.*, **34**, 1358 (1942).]

structure the "freezing" of viscous elements during rapid stress reversal is a dominant factor (Sec. 953).

1324. Variations in Dynamic Modulus and Internal Friction. If the temperature of the specimen is held constant, the dynamic modulus of a rubber appears to be essentially independent of the frequency for the range 15 to 100 cycles per second at small amplitudes. By contrast, the internal friction is nearly inversely proportional to the frequency (Fig. 13-16). At higher frequencies, *i.e.*, several hundred cycles per second; the dynamic modulus increases with rise in frequency. As would be expected from theory, both the dynamic modulus and the internal friction generally decrease rapidly as temperature increases (Fig. 13-17).

The effect of vibration amplitude on both properties varies over wide limits. For a Hevea-rubber stock loaded with 50 parts of gas black there is a considerable drop as the amplitude increases, whereas for the cor-

responding pure-gum vulcanizate strikingly little change occurs, at least in the region of small amplitudes (Fig. 13-18). As the amplitude increases (frequency constant), heat generation within the specimen increases and much of the drop in dynamic modulus and internal friction at increased amplitude is due to this heat effect.

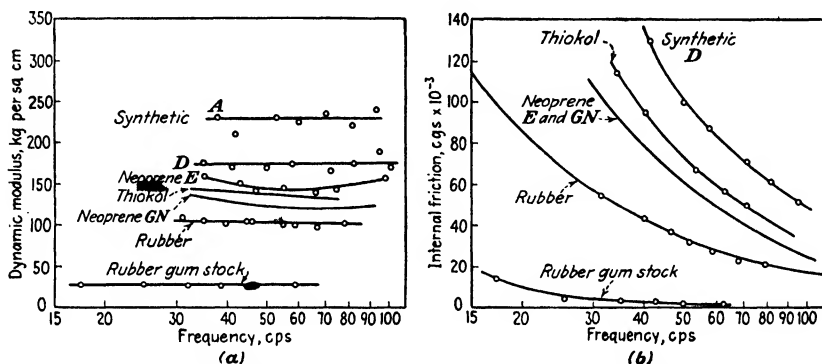


FIG. 13-16. Dynamic modulus (a) and internal friction (b) of rubbers as functions of frequency at 28°C. See Table 13-10 for identification of rubbers. [R. B. Stambaugh, *Ind. Eng. Chem.*, **34**, 1358 (1942).]

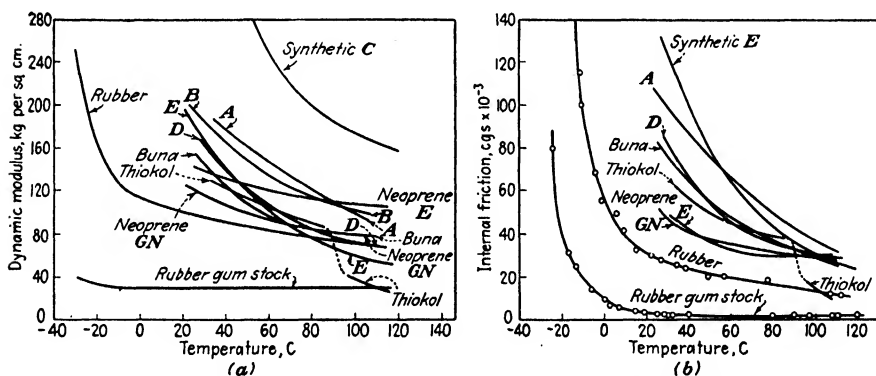


FIG. 13-17. Dynamic modulus (a) and internal friction (b) of rubbers as functions of temperature at 60 cycles per sec. See Table 13-10 for identification of rubbers. [R. B. Stambaugh, *Ind. Eng. Chem.*, **34**, 1358 (1942).]

1325. The Effects of Loading on Dynamic Properties. When Hevea-rubber vulcanizate is loaded with filler, both the dynamic modulus and the internal friction rise. Dynamic resilience as a function of loading appears in Fig. 13-19. The curves were calculated from the measured values of E_d and η_d by means of Eq. (13-1). These curves are strikingly similar to those of pendulum rebound vs. loading, and the correlation between dynamic resilience as here calculated and pendulum rebound is close (Table 13-10). The effect of loading, then, is to decrease dynamic

resilience and increase damping and heat build-up. The curves represent a quantitative measure of the reinforcing action of the several fillers and in general fall in the order of particle size.

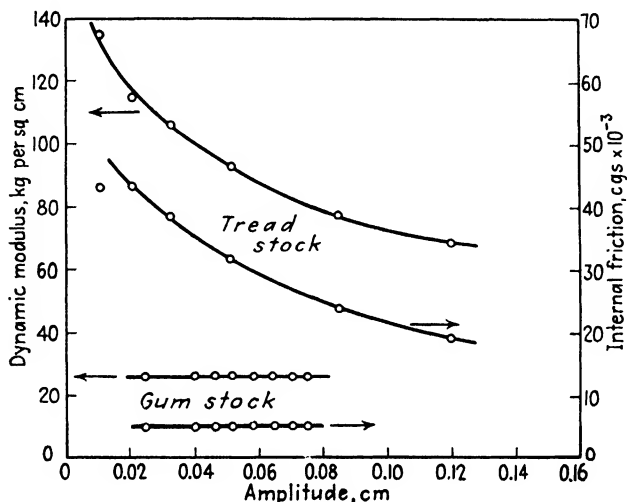


FIG. 13-18. Effect of amplitude on dynamic modulus and internal friction of Hevea-rubber stocks. [R. B. Stambaugh, *Ind. Eng. Chem.*, **34**, 1358 (1942).]

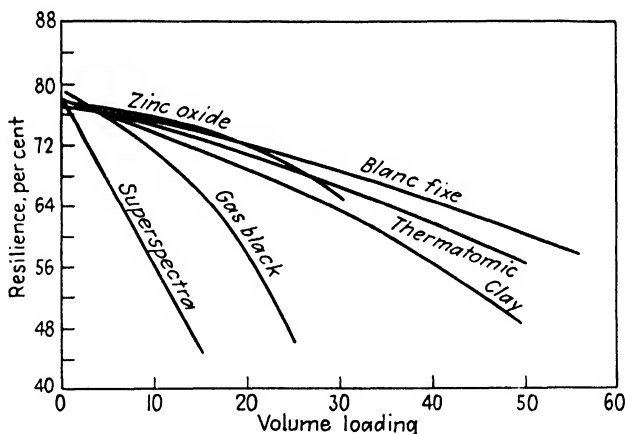


FIG. 13-19. Effect of loading on dynamic resilience of Hevea vulcanizates. [S. D. Gehman, D. E. Woodford, and R. B. Stambaugh, *Ind. Eng. Chem.*, **33**, 1032 (1941).]

Figure 13-20 shows the ratio of dynamic to static modulus as a function of loading. The relative positions of the curves are different here from those in the preceding graphs. For channel black the ratio is highly sensitive to loading, whereas for blanc fixe it is practically independent.

These data show the wide range of dynamic properties obtainable

TABLE 13-10. VIBRATION PROPERTIES OF VARIOUS VULCANIZATES

Stock	At 28 C and 60 cycles per sec			Pendulum rebound, %	Relative rate of heat generation, calculated from dynamic constants. Hevea tread stock = 100 H_x at 100 C	Heat rise in a constant-amplitude flexometer test	
	Dynamic modulus of elasticity, kg/sq cm E_d	Internal friction, cgs $\times 10^{-3}$ η_A	Dynamic resilience, % R			Actual	Relative
						deg C	Hevea tread stock = 100
Hevea-rubber gum stock . . .	29	3.0	78	18	6	8.5
Hevea rubber . .	98	26.5	52	72	100	71	100
Synthetic D . . .	171	85	30	54	164	102	144
Neoprene E . . .	127	50.5	38	65	168	97	136
Neoprene GN . .	144	48	45	60	190	115	162
Synthetic B . . .	198	102	29	51.5	210	107	151
Synthetic A . . .	225	107	32	53	222	113	160
Synthetic C . . .	572	347	23	31	374	133	187

Based on data from STAMBAUGH, R. B., *Ind. Eng. Chem.*, **34**, 1358 (1942), and private communication.

Stocks. All stocks except first are gas-black-loaded.

Synthetic A. 70:30, butadiene: acrylonitrile coagulated with barium chloride.

Synthetic B. 70:30, butadiene: acrylonitrile coagulated with alcohol.

Synthetic C. 50:50, butadiene: acrylonitrile.

Synthetic D. 60:40, butadiene: styrene, sodium oleate type.

Synthetic E. 60:40, butadiene: styrene, sodium lauryl sulfate type.

Stocks are identical with those of Figs. 13-15 to 13-17, 13-21, and 13-22. In these figures, "rubber" refers to Hevea rubber.

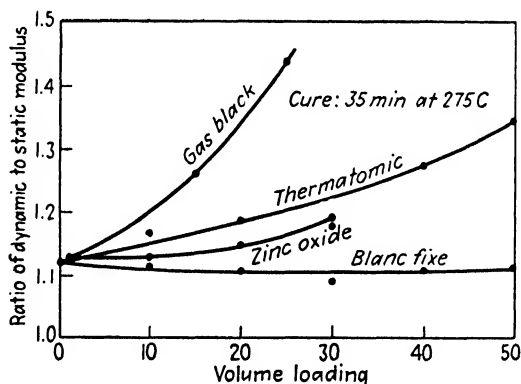


FIG. 13-20. Effect of loading on ratio of dynamic to static modulus of Hevea vulcanizates. [S. D. Gehman, D. E. Woodford, and R. B. Stambaugh, *Ind. Eng. Chem.*, **33**, 1032 (1941).]

through the loading technique and illustrate the basic principles involved in the selection of a reinforcing filler for dynamic purposes.

1326. The Dynamic Resilience and Damping Capacity. As shown by Eq. (13-1), the per cent dynamic resilience (and per cent damping) is a function of frequency, internal friction, and dynamic modulus, the last two being interdependent and affected by the frequency itself. The over-all variation of dynamic resilience with frequency (the temperature and amplitude presumably constant) is shown in Fig. 13-21. The dynamic resilience decreases at frequencies above 300 cycles per second.

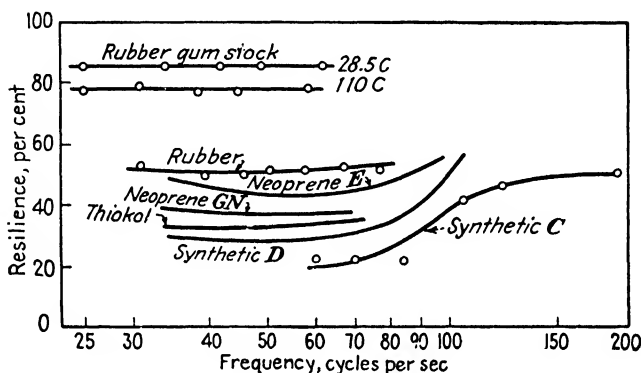


FIG. 13-21. Dynamic resilience of rubbers as functions of frequency. Temperature 28 C unless otherwise indicated. See Table 13-10 for identification of rubbers. [*R. B. Stambaugh, Ind. Eng. Chem.*, **34**, 1358 (1942).]

Of more importance is the effect of temperature (Fig. 13-22). It is here that the striking difference between the rheological behavior of rubbers and other solids such as metals, fibers, and plastics is best illustrated. Whereas the resilience of the latter decreases with temperature rise, that of rubber increases practically linearly. Put the other way around, rubber is a unique solid in that its damping capacity *decreases* with rise in temperature. This behavior is directly ascribable to its captive-liquid character. A highly crystalline elastic solid such as steel is practically devoid of viscosity; the variation of damping capacity with temperature therefore depends mainly upon the effect of temperature on the dynamic modulus. By contrast, along with elasticity rubber possesses viscosity and liquid character to an exaggerated extent. The drop in internal friction with rising temperature overshadows the effect on its dynamic modulus, and the damping capacity decreases.

At the current writing, no synthetic-rubber vulcanizate has been produced with as high a dynamic resilience as vulcanized Hevea rubber. By the same token, the vibration-damping capacities of the synthetic rubbers are superior to those of Hevea (around room temperature).

1327. Heat Build-up. A large hysteresis loop, *i.e.*, a high damping capacity, not only means the ability to eliminate vibration and to prevent the building up of high dynamic stresses in a vibrating member [Eq. (9-17, page 421)] but also leads to a high rate of heat generation, especially if the driving force or amplitude of forced vibrations is large [Eqs. (13-2) and (13-3)]. If the operating conditions are such that hysteresis heat is generated faster than it can be dissipated, the member will get hot and may fail rapidly in service. This is likely to be the case in many out-

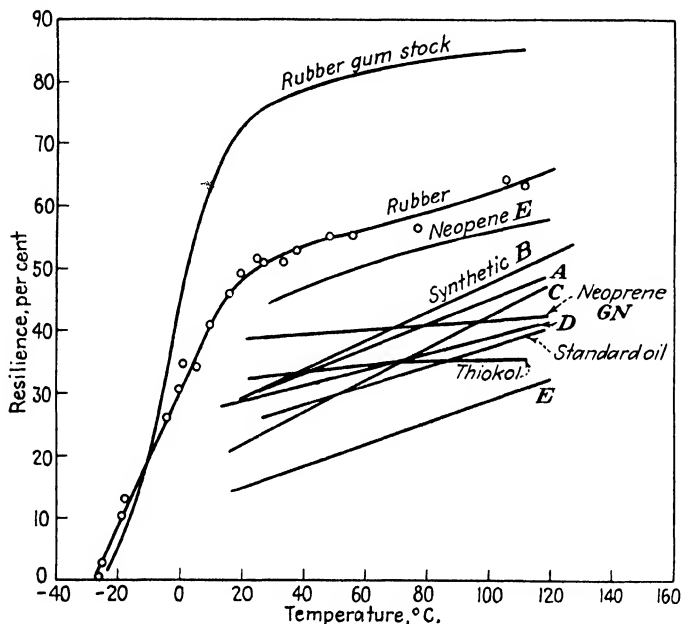


FIG. 13-22. Dynamic resilience of rubbers as functions of temperature at 60 cycles per sec. See Table 13-10 for identification of rubbers. [R. B. Stambaugh, *Ind. Eng. Chem.*, **34**, 1358 (1942).]

standingly important applications of rubber, *e.g.*, tires. In other words, in rubber, the problem is often one of too large rather than too small a damping capacity.

The rate at which heat is dissipated by a part depends upon the ambient temperature, the heat-conductivity and heat-transfer characteristics of the material, the dimensions of the member, *e.g.*, ratio of surface to volume, and many other factors. Relative rates of heat generation as calculated from Eqs. (13-2) and (13-3) tell only the relative *tendencies* toward heat build-up in a cyclically stressed member. The actual equilibrium temperature attained can be arrived at only by testing the member under conditions closely simulating those of actual service

so that the rates of both heat generation and heat dissipation are taken into account.

Flexometers for testing heat build-up under forced vibrations in compression have been developed. Test-piece thickness, frequencies, amplitudes, and driving forces are of the order encountered in tire service. (In normal times about 70 per cent of the rubber consumed in the United States goes into tires.) Figure 13-23 shows the effect of vibration amplitude on actual heat build-up. The temperature rise (ordinate) is the

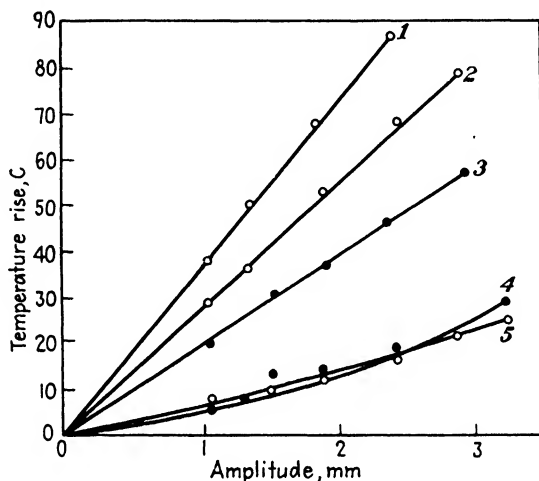


FIG. 13-23. Effect of amplitude on heat build-up of vulcanizates. Test piece 1 in. sq \times 2 in. long. Curve 1: GR-S, 20 volumes gas black. Curve 2: Hevea, 25 volumes gas black. Curve 3: Hevea, 20 volumes gas black. Curve 4: Hevea, 20 volumes zinc oxide. Curve 5: Hevea, 20 volumes thernatomic black. [S. D. Gehman, P. J. Jones, and D. E. Woodford, *Ind. Eng. Chem.*, **35**, 964 (1943).]

difference between room temperature and the equilibrium temperature attained in the cyclically stressed test specimen. Several important points are illustrated. First, there is the magnitude of the effect itself. Such temperature rises in tire rubber may cause considerable damage. Second, the heat build-up in the synthetic rubber is considerably higher than that in the corresponding Hevea-rubber tread stock. Third, the heat build-up increases as the reinforcing power of the filler increases. Finally, although from Eq. (13-3) the rate of heat generation would seem to increase as the *square* of the amplitude, as the temperature rises, resilience increases and modulus decreases. Furthermore, the rate of heat *dissipation* increases at higher temperatures. The over-all result is that the actual relation between heat build-up and amplitude is approximately linear as shown in the figure.

H_s values calculated from Eq. (13-3) generally follow the same order

as actual heat build-up, but the correlation is by no means quantitative (Table 13-10). It cannot be expected to be, for reasons cited above.

Equations (13-2) and (13-3) involve a highly significant point. If stocks are compared for vibrations at constant driving force F , a high dynamic modulus leads to a *low* relative rate of heat generation, whereas for vibrations of equal amplitude it results in a high relative rate. It is thus extremely important to know whether a cyclic deformation occurring in a rubber part during service is of the constant-force or the constant-amplitude type.

In a pneumatic-tire tread the conditions of deformation are complicated. For example, bending of the wall during road use is essentially a constant-amplitude deflection relatively independent of the stiffness. By contrast, pressure between the road and the tire involves a constant-force compression cycle that will vary inversely with the stiffness. Under such conditions, the actual relative heat build-up in road use will not show the same spread of values as will be exhibited by constant-amplitude flexometer tests in the laboratory. To evaluate tread stocks completely, constant-force as well as constant-amplitude flexometer tests should be run. For solid tires a constant-force comparison would be much more significant than a constant-amplitude test. Resiliometer tests in which a tire is run in contact with a wheel acting as the road seem to indicate that constant-amplitude flexometer comparisons rate pneumatic-tire treads in the correct order of heat build-up but exaggerate the differences between them.

Up to the current writing, all synthetic-rubber tread stocks exhibit greater heat build-up than Hevea treads.

1328. Flex Failure. Rubber vulcanizates develop cracks when subjected to a sufficient number of stress cycles. This fatigue failure is a limiting factor in the service life of such items as tires and power belting. Like all fatigue failures, that of a rubber vulcanizate is intimately associated with creep and relaxation and is a complicated process influenced by many variables (Sec. 956). Rubber, with its high damping capacity, undergoes considerable heat build-up, which catalyzes oxidative reactions that are prominent determinants of its physical deterioration. (This is discussed in the next section.) Since damping capacity, dynamic modulus, and internal friction are all intimately associated with temperature changes and the magnitude and frequency of the cyclic stresses and strains, it follows that the fatigue failure of a rubber specimen will be especially dependent upon the conditions of test. To cite one instance, it has been found that under certain test conditions the number of cycles required to break a rubber test piece which does not return to zero elongation during cyclic stressing is four to ten times that required when

it does. In one standard laboratory test, plasticized polyvinyl chloride was still serviceable after 3,000,000 cycles where rubber vulcanizates failed as follows: butyl, 185,000; Hevea, 45,000; buta S, 22,000; buta N, 7,500. But unless the test conditions are reasonably close to those of actual service, such measurements might not even rate the products in their proper order, let alone give a quantitative estimate of their service flex life.

CREEP AND RELAXATION

1329. Creep and relaxation rates of rubber are high even in the vulcanized state. The compression-set test is often used for comparative

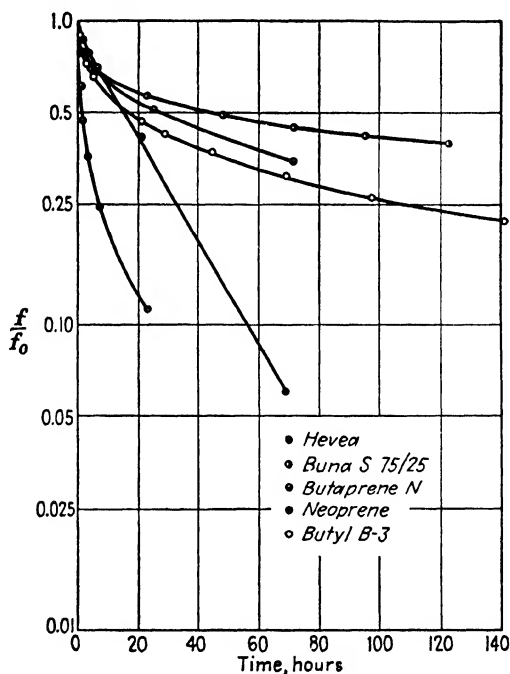


FIG. 13-24. Relaxation of stress in gum stocks at constant elongation; 100 C, 50 per cent elongation. Ordinate is ratio of stress after time lapse to initial stress. [R. D. Andrews, R. S. Mesrobian, and A. V. Tobolsky, *Trans. Am. Soc. Mech. Engrs.*, **67**, 569 (1945).]

evaluation. Studies of the creep and relaxation of rubber vulcanizates at elevated temperatures are important to many practical applications. In addition, such studies permit a new approach to and interpretation of the physical deteriorations known collectively as aging.

1330. Continuous Relaxation under Stress. Figure 13-24 shows the continuous-stress-relaxation curves of various pure-gum vulcanizates held at a constant elongation. It is seen that the relaxation rates are quite

different, the neoprene relaxing fastest, the buna S (buta S) slowest. Other facts that have been discovered about these curves are as follows:

1. The relaxation rate may be reduced a thousandfold by the rigorous exclusion of oxygen.
2. The presence of certain antioxidants reduces the relaxation rate.
3. The relaxation curve is relatively independent of elongation up to high elongations.
4. The relaxation curve is only slightly altered by the presence of carbon black in the vulcanizate.

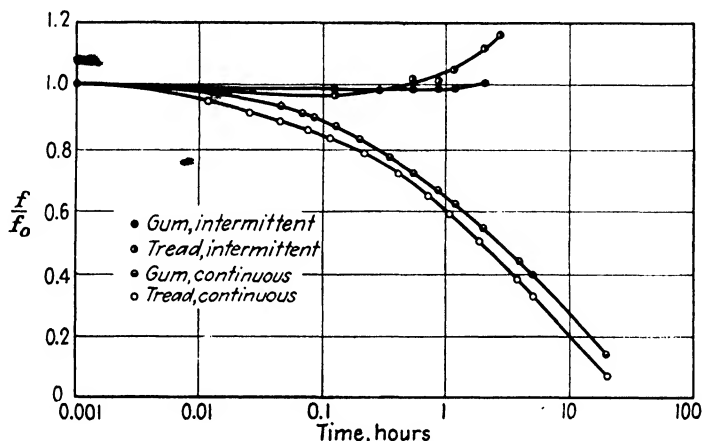


FIG. 13-25. Continuous and intermittent stress relaxation in GR-S stocks; 130 C, 50 per cent elongation. [R. D. Andrews, R. S. Mesrobian, and A. V. Tobolsky, *Trans. Am. Soc. Mech. Engrs.*, **67**, 569 (1945).]

5. The type of vulcanization, *i.e.*, sulfur or nonsulfur, is of less consequence than the polymer type.

6. The relaxation of Hevea-gum vulcanizate follows a simple exponential decay law. That of other rubbers may be fitted to a sum of exponential decay terms.

These facts indicate that relaxation under stress takes place as a result of oxidative rupture of chain sections.

1331. Intermittent Relaxation. If the *intermittent-relaxation* curve of a vulcanizate is also determined, the results are interesting. In such a study, the specimen is left at rest at the experimental temperature except that it is momentarily stretched to a fixed elongation at periodic intervals, the stress required to reach this elongation being recorded at each observation. The intermittent-stress-relaxation curve is thus a measure of the physical deterioration of rubber exposed to heat and oxygen in an unstressed condition. Figure 13-25 shows both the intermittent- and continuous-relaxation curves for buta-S stocks. It will be

seen that, for this rubber, the intermittent-relaxation curve shows that the modulus *increases* continuously with time of heating. Neoprene and buta-N vulcanizates behave similarly. By contrast, butyl rubber exhibits a continuous *decrease* in modulus, whereas in Hevea there is an initial decrease followed by a subsequent rise. A rise in modulus on heating points strongly to a cross-linking or vulcanizing reaction taking place.

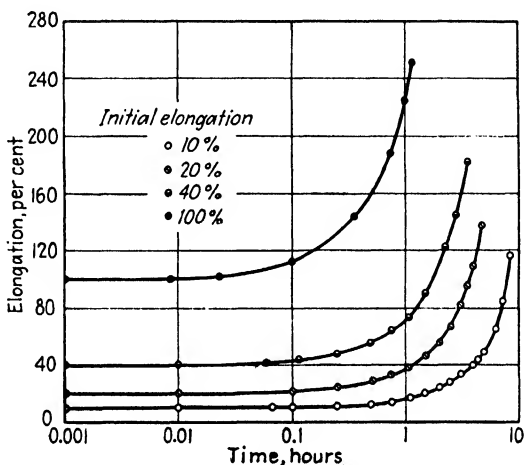


FIG. 13-26. Creep of Hevea-gum vulcanizate at various elongations; 120 C. [R. D. Andrews, R. S. Mesrobian, and A. V. Tobolsky, *Trans. Am. Soc. Mech. Engrs.*, **67**, 569 (1945).]

1332. Creep. The final step in the study is the determination of the rate of creep under constant stress. Figure 13-26 presents a set of creep curves for a Hevea-gum vulcanizate, starting at different initial elongations.

If it is assumed that relaxation under stress is attributable to chemical reactions which result in chain rupture, it is reasonable to suppose that these same reactions are responsible for creep. A theoretical analysis of data such as the above indicates that creep and relaxation should be related as follows:

$$\frac{f}{f_0} = \frac{(l_0/l_u) - (l_u/l_0)^2}{(l/l_u) - (l_u/l_0)^2} \quad (13-5)$$

where f/f_0 is the fraction of the original stress at time t in a relaxation experiment, l is the length at time t in a creep experiment, l_0 is the initial length, and l_u the unstretched length. It is useful to define the right-hand side of Eq. (13-5) as the creep function. In Fig. 13-27 the validity of this equation is demonstrated for Hevea-gum stocks; the creep data of Fig. 13-26 are replotted in terms of this creep function and shown as

points on the graph; the experimental continuous-stress-relaxation curve for the same stock at the same temperature is shown as a full line.

1333. Correlation of Creep and Relaxation with Rubber Aging. It will now be shown how these creep and relaxation studies may be used to elucidate the deteriorative changes occurring in rubber vulcanizates.

The data presented in Figs. 13-24 to 13-27, along with the six additional facts relating to stress relaxation listed in Sec. 1330, indicate very strongly that the physical deterioration of rubber vulcanizates by heat and oxygen depends on two competing reactions—a rupture of chain

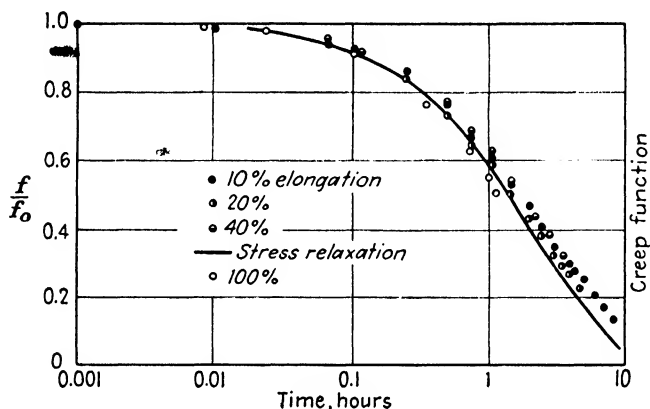


Fig. 13-27. Comparison of creep function with continuous stress relaxation for Hevea-gum vulcanizate at 120 C. [R. D. Andrews, R. S. Mesrobian, and A. V. Tobolsky, *Trans. Am. Soc. Mech. Engrs.*, **67**, 569 (1945).]

sections and a cross-linking reaction. The fact that these reactions appear to occur at comparable rates over a wide range of temperature suggests that they are intimately related and that there may be a single activation step common to both.

For a cross link to form in a rubber network, two reacting structures must “find” each other and come into juxtaposition. This is more likely to happen in an unstressed portion of the rubber mass, where chain sections are freer to undergo local kinetic motions. The measurement of relaxation under stress at constant extension (Fig. 13-24) therefore probably provides a means of isolating the effect of the chain-rupture reaction from that of the cross-linking reaction since, if the latter takes place preferentially in relaxed positions within the stressed mass, the new cross-links as they form will not contribute toward resistance of the external stress. The decay of stress (relaxation) is thus presumably attributable to the rupture of stressed chain sections. According to theory (Sec. 1227), the original stress is proportional to the concentration

of principal chain sections. Consequently, the rate of relaxation is proportional to the rate of chain rupture (of principal chain sections).

As previously stated, the intermittent-relaxation rate is a measure of the changes occurring when *unstressed* rubber is heated. In terms of the theory now under discussion, the change of retractive force with time as determined by intermittent relaxation is a measurement of the *net rate* of both chain rupture and cross-linkage. If this be true, the intermittent-relaxation curve should never decrease as rapidly as the continuous-relaxation curve. This is indeed the case (Fig. 13-25). For some stocks such as neoprene, buta N, and GR-S, the resistance to stress increases with time of heating, which is taken to mean that cross-linkage is occurring at a greater rate than chain rupture. In others like butyl and Hevea, chain scission is predominant, and the modulus steadily decreases.

Figure 13-27 shows that for Hevea-gum vulcanizates the creep function is nearly identical with the continuous-relaxation function. This is also the case for butyl rubbers and other vulcanizates that soften during high-temperature aging. On the other hand, creep is decidedly slower than relaxation for GR-S as well as for other vulcanizates that harden rather than soften at elevated temperatures. It is also found that the deviation between creep and relaxation is greater in tread stocks than in the corresponding gum stocks. Equation (13-5) was derived on the assumption that creep is attributable entirely to the chain-rupture reaction. This is essentially so since new cross-links tend to form preferentially in relaxed elements of the structure. Nevertheless, as creep progresses, the newly formed cross-links will exert some retarding action and in vulcanizates where the cross-linking action is marked the creep rate is somewhat slower than the relaxation rate. Despite these differences, the continuous-relaxation curves of rubber vulcanizates are adequate for comparing the rates of oxidative chain rupture in various stocks.

These studies are of prime interest both in theory and in practice. The simple and direct way in which these measurements of creep, relaxation, and modulus may be correlated with the postulated changes in molecular structure lends substance to the whole theory of rubber aging (Sec. 1317). Application of these experimental methods may eventually facilitate a more exact elucidation of the "building-up" and "tearing-down" processes accompanying sulfur vulcanization (Sec. 1307) and should also be found generally applicable to the exposition of creep, relaxation, and embrittlement of three-dimensional polymers other than rubbers.

The practical implications of these studies are immediate and far-reaching, as will be gathered from a few examples. The measurements described above are all made on thin specimens to permit ready penetra-

tion by oxygen and hence homogeneous oxidation. When thick articles are to be used in actual service, all measurements of aging effects should be made on similarly thick specimens if the test results are to be meaningful. The great differences between the continuous- and intermittent-relaxation curves point out that the failure of a rubber part in service will depend very much on whether it is subjected to continuous or intermittent stress. Under the same conditions of environment and temperature, it is quite possible that vulcanizate *A* will greatly outlast vulcanizate *B* under continuous stress, while exactly the opposite may obtain under momentary intermittent loadings. The results of oven tests and oxygen-bomb tests must therefore be interpreted with caution, and at best only gross differences in results may be counted on to reflect real differences in actual service performance. The same may be said of laboratory flexometer and fatigue tests. The creep and relaxation studies described above confirm conclusions previously reached, *viz.*, that laboratory flexometer and fatigue tests must be conducted under conditions closely approaching those of service if the results are to have even semiquantitative meaning.

A cross-linked rubber vulcanizate swells in a liquid hydrocarbon but is said to be "insoluble" in it. Nevertheless, on long-time immersion it often disintegrates, a large fraction of the rubber eventually going into solution. Since, as described in Sec. 1225, the principal chain sections of a swollen vulcanizate are under continuous tension, this ultimate breakdown in a solvent is a creep failure interpretable in terms of the same creep and relaxation mechanisms that account for physical deterioration under ordinary mechanical stress.

OTHER MECHANICAL PROPERTIES

1334. Space does not permit the detailed discussion of many mechanical properties that are vital to the service life of rubber products. Among these are resistance to abrasion and tear, flex fatigue, embrittlement and attendant loss of rubberiness, and damping capacity at subnormal temperatures. However, some information on these properties is included in various discussions through the text. For example, brittle points (Sec. 519) serve as an approximate guide to performance at subnormal temperatures.

GAS PERMEABILITY

1335. The diffusion of many gases such as air, hydrogen, helium, nitrogen, water vapor, and sulfur dioxide takes place at a lower rate through synthetic rubbers than through Hevea. For example, the permeability to hydrogen increases in the following order: plasticized polyvinyl chloride, thiokol, butyl, neoprene, buta N, Hevea. The com-

bination of tear resistance, resistance to aging, and low permeability to air renders butyl rubber particularly attractive for the inner tubes of pneumatic tires. Low gas permeability coupled with stability under direct sunlight has led to the replacement of Hevea by synthetic rubbers in the manufacture of envelopes for balloons and dirigibles.

LATEX PROCESSING

1336. Hevea rubber occurs as a natural latex, and synthetic rubbers are produced as latices by emulsion polymerization. Nowhere does emulsion processing (Sec. 843) afford more attractive possibilities than in the field of rubber technology, as may be gathered from the following procedural outline.

A Hevea-rubber latex from the tree is concentrated and freed of a large part of its nonhydrocarbon impurities by the process of centrifuging, or *creaming*. Stabilizing agents are added. It is not difficult to produce stable latices with a total solids content of 40 to 60 per cent or more. The concentrated emulsion, in spite of its high solids content, has a relatively low viscosity and flows readily. Through the use of effective wetting and stabilizing agents, liquid and powdered-solid compounding ingredients of all sorts such as vulcanizing agents, accelerators, fillers, and activators may be incorporated into the latex to form uniform and stable dispersions of vulcanizable mixes (Table 8-1). All this processing is conducted at or near room temperature with simple mixing equipment. With a total solids content of 60 per cent or more the mix is still fluid enough to pour, spread, and penetrate readily and can be used as a vulcanizable adhesive, cement, or waterproofing compound. It may be handled by the techniques of spraying, dipping, and electrodeposition (Secs. 844 and 845). Since the solids content is high compared with that of a true solution of rubber, less redipping or respraying is necessary to build up a desired thickness.

In all the above processing and manipulation there has been no degradation of the rubber hydrocarbon since the costly and damaging step of milling has been eliminated and there has been no exposure to elevated temperatures. This being the case, ultraaccelerators may be used since there is no danger of scorching (premature vulcanization), and thus it is possible to vulcanize the goods rapidly at low temperatures (100 C or even lower). This again minimizes degradative action on the binder. For these combined reasons the average molecular weight of the primary rubber chains remains high, and it is possible to produce latex-processed pure-gum vulcanizates with excellent mechanical properties [Eq. (12-36)]. For example, tensile strength may be as high as 4,000 psi with an elongation at break of 1,000 per cent, as compared with

3,000 psi and 700 per cent elongation for a conventionally milled and processed pure-gum Hevea vulcanizate. Other advantages of low-temperature vulcanization are that it obviates the need for (steam) pressure vulcanizers and permits the use of bright dyes, which discolor at ordinary vulcanizing temperatures.

It might be thought that exceptionally strong latex-processed Hevea vulcanizates might be made by the incorporation of carbon black. However, this is not so. All fillers added to latex-processed Hevea rubber are inert, lowering rather than raising the tensile strength. Evidently the nonuniform Hevea latex globules (Sec. 1301) are not ruptured during latex processing. The filler particles surround rather than penetrate them. As a consequence, reinforcement does not take place, and high tensile strength and tear resistance do not ensue. This disadvantage may be partly overcome by coagulating the compounded latex and subjecting the crumb to a short milling. However, this tends to vitiate one of the main advantages of latex processing. The globules of synthetic rubber latices are much smaller and less differentiated than those of Hevea latex, so that some reinforcement by carbon does occur.

The molding of thick, solid, nonporous articles from a compounded latex is virtually impossible because of the difficulty of removing water from the mass. However, nonporous thin moldings are entirely possible. Furthermore, latices are admirably suited to the production of expanded materials (Sec. 853).

REFERENCES

GENERAL

See references at end of Chap. 12.

See also Appendix A.

PARTICULAR TOPICS

See references accompanying tables and figures of this chapter.

Latex Processing

FLINT, C. F., "Chemistry and Technology of Rubber Latex," D. Van Nostrand Company, Inc., New York.

CHAPTER 14

SURFACE COATINGS

1400. The surface is what normally meets the eye. It may please or displease the beholder. "Save the surface and you save all" is one of the most striking advertising slogans ever devised. The two main functions of surface coatings are decoration and protection. Often these functions are combined. The organic surface coatings called paints, varnishes, and lacquers are of the order of 1 to 2 mils thick, and it is upon these thin films that such great reliance is placed to beautify our surroundings and retard the ever-active forces of corrosion and decay.

In these two-dimensional films, surface forces and phenomena are prime considerations; and since they are usually expected to have a protracted service life, long-time chemistry also is a vital factor. An inherent characteristic of organic surface coatings is that complex combinations of high polymers and resins are used in their manufacture. It is the object of this chapter to present important general phases of the subject rather than to discuss a great number of specific products.

FUNDAMENTAL TYPES OF SURFACE COATING

1401. Surface coatings are applied as fluid dispersions and must dry to thin, continuous, adherent solid films. Depending on the mechanism involved in drying they are of two fundamental types.

1. *Lacquer-type coatings.* These are distinguished by the fact that drying involves merely the evaporation of the solvents and thinners originally present. No chemical reactions accompany the drying. All polymeric constituents are present in fully polymerized form at the time of application.

2. *Varnish-type coatings.* In these, drying involves not only the evaporation of solvents but also polymerization reactions, which lead to the formation of molecules in the dried film that are larger and often different from those present at the time of application.¹

Surface coatings may be further subdivided into straight air-drying types, which dry at ordinary room conditions, and baking types, which require elevated temperatures. As might be expected, lacquer types are generally quicker drying than varnish types.

¹ It is unfortunate that certain products such as solutions of shellac in alcohol are called *spirit varnishes* although they are definitely lacquer-type coatings.

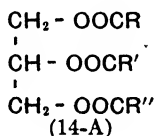
A *paint* is a mixture of opaque or semiopaque solid substances with liquids, suitable for application to surfaces by brushing, spraying, or dipping and of such nature that it eventually dries or solidifies to an adherent coating. Paints may be either of the lacquer or of the varnish type.

An *enamel* is characterized by the fact that it dries to a film of outstanding hardness. Enamels also may be of either the lacquer or the varnish type. There is no sharp dividing line between paints and enamels. It may be said in general that a typical paint is low in or devoid of hard resinous constituents, while an enamel contains an appreciable amount of these.

OLEORESINOUS VARNISHES

1402. An *oleoresinous varnish* contains drying oil, resin, driers, solvents, and thinners, with or without pigment and color. A typical clear varnish mix is presented in Table 8-1.

1403. Composition of Drying Oils. Animal and vegetable oils consist of mixtures of mixed triglyceryl esters of fatty acids [structure (14-A)].



R, R', R'' represent straight-chain saturated or unsaturated hydrocarbon radicals. Oils may be nondrying, semidrying, or drying. The "drying" of an oil in air is accompanied by the following: (1) absorption of oxygen, (2) decrease in iodine number, (3) decrease in diene number, (4) decrease in solubility, (5) increase in average molecular weight, and (6) progressive increase in viscosity until finally the liquid has changed to a tough, somewhat rubbery solid. In other words, the drying of an oil is a polymerization process involving gelation. Saturated oils do not dry. Drying properties of oils are more pronounced with increase in the total unsaturation and, what is more important, increase in the number of conjugated double bonds in the fatty acid radicals. For example, monoolefinic acids such as oleic are not active in the drying process. The seat of rapid, effective drying is the di-, tri-, and tetraolefinic acid esters, especially, as already mentioned, those in which the olefinic bonds are conjugated.

Upon hydrolysis, drying oils usually yield 90 per cent or more of unsaturated acids. These are chiefly 18-carbon-atom straight-chain acids, and there is a striking uniformity in their structures, many containing the grouping $-(\text{CH}_2)_7\text{COOH}$, as shown in Table 14-1.

Table 14-2 gives the compositions of several semidrying and drying oils.

Consideration of Tables 14-1 and 14-2 indicates why a tung oil dries faster than a linseed oil having the same total unsaturation.

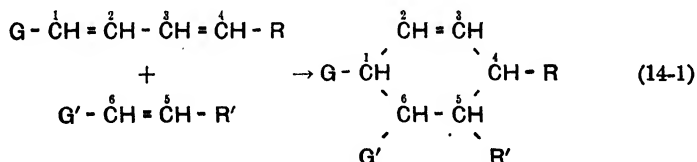
TABLE 14-1. STRUCTURES OF UNSATURATED FATTY ACIDS COMMONLY PRESENT IN THE TRIGLYCERIDES OF OILS USED FOR VARNISHES

Acid	Structure
Oleic.....	$\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$
Ricinoleic.....	$\text{CH}_3(\text{CH}_2)_8\text{CHOHCH}_2\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$
Linoleic.....	$\text{CH}_3(\text{CH}_2)_4\text{CH}=\text{CHCH}_2\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$
Linolenic.....	$\text{CH}_3\text{CH}_2\text{CH}=\text{CHCH}_2\text{CH}=\text{CHCH}_2\text{CH}=\text{CH}(\text{CH}_2)_4\text{COOH}$
Eleostearic.....	$\text{CH}_3(\text{CH}_2)_3\text{CH}=\text{CHCH}=\text{CHCH}=\text{CH}(\text{CH}_2)_7\text{COOH}$
Licanic.....	$\text{CH}_3(\text{CH}_2)_3\text{CH}=\text{CHCH}=\text{CHCH}=\text{CH}(\text{CH}_2)_4\text{CO}(\text{CH}_2)_2\text{COOH}$

TABLE 14-2. COMPOSITIONS OF SEVERAL SEMIDRYING AND DRYING OILS

Oil	Glyceride composition, %				
	Saturated and mono-olefinic acids	Linoleic and other diolefinic acids	Linolenic acid	Eleostearic acid	Licanic acid
Corn.....	58	42
Soybean.....	40	56	4
Linseed.....	31	24	45
Dehydrated castor.....	16	84
Perilla.....	15	38	47
Tung.....	20	80	..
Oiticica.....	18	82

1404. Reactions Involved in Drying. Most varnish mixes contain several resinous and polymeric constituents, which are cooked together at elevated temperatures in a varnish kettle. When drying oils are heated to 250 to 300 C, even in the absence of oxygen, polymerization takes place. This nonoxidative polymerization is often called *thermal polymerization* or heat bodying. It has been established that the modified Diels-Alder reaction [Eq. (4-41)] is involved.



In Eq. (14-1), G represents the glycerol end of a fatty acid chain. Studies of the heat-bodying reaction indicate that nonconjugated systems of

double bonds such as those originally present in linoleic and linolenic radicals (Table 14-1) often undergo rearrangement to conjugated structures [Eq. (4-27), page 119], after which the cyclizing cross-linkage of Eq. (14-1) occurs.

Two or even three cyclic linkages may form between a single pair of fatty acid chains provided that sufficient unsaturation is available. Since reaction (14-1) may take place between fatty acid radicals on different triglyceride molecules, space polymerization may result. There is an increase in viscosity and if the bodying is permitted to go too far, gelation takes place in the kettle. At the same time, the cyclization draws the triglycerides together into a denser molecular structure, and the degree of unsaturation decreases.

Oil bodying is usually accompanied by a certain amount of glyceride decomposition, free fatty acids being formed. These acids must be regarded as an integral component of the bodied oil since they play an effective role in the reactivity of the oil toward basic pigments and resin constituents. The amount of acid present is usually expressed as the acid number. Free acidity retards the polymerization reactions taking place in the kettle. If it is not excessive, this often presents an advantage in that the danger of sudden gelation during varnish cooking is minimized.

Unsaturated bonds are still present in a bodied oil; and if a thin film is exposed to air at room temperature, especially in the presence of catalysts called *driers* (oil-soluble compounds of cobalt, manganese, and lead), oxygen is absorbed and a further polymerization takes place, resulting ultimately in a solid, dried film. The mechanism of this *oxidative drying* has not been fully established. It appears that peroxides first form, which later rearrange into other oxygen compounds. Oxygen absorption is an essential concomitant of the reaction, and it is an established fact that in this process oxidation precedes and initiates polymerization. Most of the evidence indicates that the ultimate result is carbon-to-carbon cross-linkage either via vinyl addition or by cyclizations similar to those occurring in heat bodying. The Diels-Alder reaction may be involved [Eq. (4-37), page 132]. At any rate, the dried film is a mutaplast of pronounced hydrocarbon character and very poor symmetry, which account directly for its toughness, flexibility, and somewhat rubbery character.

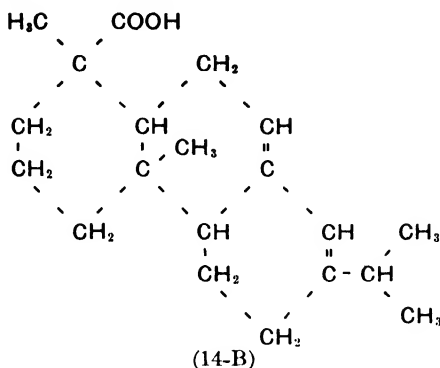
Although those oils which contain the largest amount of conjugated unsaturation have the advantages of drying fastest to the densest molecular structure, they suffer a shortcoming in that they discolor during drying to a considerably greater extent than the less highly conjugated oils. It is for this reason that in clear varnishes and white paints and enamels some drying speed is often sacrificed for better color by intro-

ducing soybean, dehydrated castor, or other comparatively slow-drying oils into the mix.

In summary, then, oils may dry by two main mechanisms, nonoxidative, or thermal, polymerization, and oxidative polymerization. Thermal polymerization is favored by high temperatures (heat bodying or baking), particularly in the absence of driers such as cobalt salts, which strongly catalyze oxidation. It is also favored if polymerization accelerators such as straight phenolic resins are present. Furthermore, it may be mentioned that this reaction tends to predominate in the drying of coatings containing large amounts of tung or other highly conjugated oil. By contrast, oxidative drying is favored by low temperatures (ordinary room conditions), especially when strong oxidation catalysts or large amounts of *any* drier are present. Linseed and similar oils tend to dry by this mechanism. *Nonoxidative polymerization results in films of greater durability and chemical resistance than oxidative drying.* Oxidation products are reactive and tend to undergo saponification and decomposition. They also impair the continuity and homogeneity of the varnish film and thus reduce its service life. Finally, in clear and white varnish types of coatings, drying speed is often sacrificed for better color.

1405. Varnish Resins. Coatings made from drying oils alone may be tough, flexible, and weather-resistant but lack hardness and gloss and require a long time to dry. To arrive at a proper balance of properties it is necessary to add more or less of a hard resin, which may be a natural resin or fossil gum like rosin, copal or dammar, or a synthetic product such as a phenolic or alkyd resin. Too much resin, however, results in a brittle film. The *oil length* of an oleoresinous varnish is the number of gallons of drying oil per 100 lb of resin. A *long-oil varnish* is tough and durable and more suitable for outdoor applications. A *short-oil varnish* is harder and more brittle and takes a higher polish, making it more suitable as a furniture finish.

The natural gums and resins that have been used for centuries as surface-coating constituents are not polymeric. Rather, they are comparatively large nonpolymeric molecules of such irregular structure and poor symmetry that they do not crystallize well. For example, the chief constituent of common rosin is abietic acid, $C_{19}H_{29}COOH$. This resinous molecule has a molecular weight of 282 and has the cumbersome structure shown in structure (14-B). Physically the fossil gums and resins are hard and glassy. (When the phenol-aldehyde polymers were developed early in the twentieth century, they were termed resins because of physical resemblance to these materials. The result is that the term is now also applied to many synthetic high polymers.)



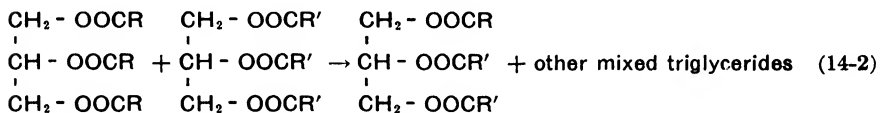
The most plentiful natural resin is common rosin (colophony). Raw rosin is not a good varnish constituent. It crystallizes slowly, forming minute cracks in the film. Its acidity is so great that it results in *bloom*, a bluish, veil-like discoloration of the coating. There is another deleterious effect of excessive acidity. Abietic acid and free fatty acids react with alkaline pigments such as zinc oxide, red lead, white lead, and litharge to form soaps. If this soap formation is too extensive, *livering* of the varnish may result; the viscosity increases until the mix has the consistency of a livery solid, in which condition it cannot be properly applied to a surface. Excessive soap formation may also cause pronounced cracking and rapid deterioration in paint films after application. This is especially true of lead paints.

One method for reducing the acidity of rosin is to add lime to the cook, forming the calcium salt called *limed rosin*. A still better method is to esterify it with glycerol in the absence of air. The resulting product is called *ester gum*. Ester gums of different acid numbers are standard items of trade. Rosin may also be esterified with glycol.

Many of the natural resins contain monocarboxylic and dicarboxylic acids as well as hydroxy acids and esters. They must be given a vigorous cook to render them compatible with and soluble in varnish oils. The main reaction is probably esterification between the hydroxyl group of one molecule and the carboxyl of another, with attendant decrease in acidity and increase in average molecular weight. For example, if raw copal having an acid number of 140 and a molecular weight of 400 is heated rapidly ("run") to 300 C, the acid number decreases to about half, corresponding to a molecular weight of about double.

The natural resins may also be rendered soluble by mastication, via a drastic mechanical working, usually on steam-heated roller mills. This has an advantage over cooking in that a greater number of functional groups are preserved and left available for reaction and linkage with drying-oil or glycerol molecules.

1406. Ester Interchange. Cooking of Varnish Mixes. If two or more uniform triglyceryl esters are heated together at about 225 C, it will be found on analyzing the product that acid radicals have migrated from one molecule to another. Reaction (14-2) is called *ester inter-*



change and is of great technical importance. Evidently the alcohol groups of a glycerol molecule will react with any carboxyl group, and an equilibrium mixture results from interchange. As previously mentioned, many of the varnish resins contain carboxyl and ester groups. If one of these resins is heated with a drying oil at the elevated temperatures employed in varnish cooking, ester interchange is often found to have taken place. Glycerol acts as a bridge through which mixed esters of oil acids and resin acids form. In addition, bifunctional dicarboxylic-resin molecules cause polymerization to take place, thus contributing to an increased molecular weight and higher viscosity. In other words, they contribute to the bodying of the batch. Finally, it is often the case that more than one drying oil is used in a varnish mix. Cooking again leads to ester interchange. *The result of ester interchange, then, is a uniformity of molecular composition not possessed by raw, uncooked physical mixtures of the several ingredients.*

Raw tung oil dries to a wrinkled, frosty, cheeselike film. This may be attributed to the very extensive chemical and physical changes that accompany drying, *viz.*, molecular densification due to cyclization, and conversion from the liquid to the solid state. Cooking the oil in the kettle partly completes these changes *before* the coating is applied. Hence the oil will be nearer the final "set" form, and the varnish will dry not only more rapidly but more uniformly and with less wrinkling. This is in many ways analogous to converting an A-stage binder to the B-stage before molding so as to reduce the time and extent of reaction required to reach the C-stage in the mold.

Ester interchange takes place at the comparatively low kettle temperature of 220 to 240 C. In this range it proceeds faster than thermal polymerization. This important point should be borne in mind when a mixture of tung and linseed oils is to be bodied. If the cook is heated immediately to a high kettle temperature (250 to 300 C), the main reaction is polymerization of the tung oil, resulting in a dispersion of highly polymerized tung oil in low-viscosity linseed. Such a mixture would not dry evenly. Good practice calls for first holding the temperature below 250 C for a few hours to enable ester interchange to take place and

only then raising the temperature to effect polymerization of the uniform mixed glycerides.

In summary, the cooking of varnish mixes is accompanied by ester interchange and heat bodying, resulting in products that dry more rapidly and more uniformly to films of greater durability and more permanent gloss. Ester interchange is important not only in oleoresinous varnishes but also in many combinations of resins and plasticizers employed in cellulose nitrate lacquers. A typical example is the cooking of maleic acid resins with dibutyl phthalate.

1407. Driers. The drying of varnishes is catalyzed by certain polyvalent metals, notably cobalt, manganese, and lead. To be effective they must be in solution in the oleoresinous mix, usually in the form of soaps such as linoleates or other oil-soluble salts like cobalt naphthenate and lead resinate (made by reacting litharge with rosin). The drier salts may be added as such, or they may be formed during the cook by adding the metal oxides and allowing them to react with the acidic constituents of the oil and resin.

There is a great deal still to be learned about drier reactions, although certain fundamental facts have been established. Those metals which catalyze oxidation also catalyze drying by polymerization, but their efficiencies in these respects differ greatly. For example, cobalt is a powerful catalyst for oxidation but comparatively weak for the polymerization reaction. The reverse is true for lead. In tung-oil varnish and phthalic-resin films, catalysis of oxidation induces wrinkling, whereas catalysis of polymerization promotes the formation of smooth films of good gloss. For such reasons, combinations of cobalt, manganese, and lead driers are more effective than any one used singly and are almost invariably employed.

The action of driers is intensified by small amounts of peroxides, although the latter do not themselves act as drying catalysts in the absence of driers. The most common method of introducing peroxide is through the addition of turpentine or dipentene, both of which normally contain small amounts thereof.

1408. Varnish Solvents. Solvents must be added to a varnish to reduce the viscosity to a point suitable for brushing. They are also added to promote good flow characteristics and to prevent "skinning." Solvent power and the ability to reduce viscosity are the most important criteria for a varnish solvent. Turpentine is still considered the most nearly ideal solvent for oleoresinous varnishes and paints. It serves as a yardstick for competing solvents.

Among the powerful varnish solvents are turpentine, dipentene, and various trade-marked special terpenes and the coal-tar solvents toluene,

xylene, and high-flash naphtha. Among the less powerful but nevertheless highly useful and widely employed solvents are mineral spirits, "V.M. and P. naphtha," and modified solvents of petroleum origin such as hydrogenated naphthas. The aromatic content of the solvents of petroleum origin is indicated by their ability to dissolve kauri gum. This, in turn, is taken as a measure of their varnish-solvent power.

Although solvents are an essential ingredient of varnishes, they play a still more important role in lacquers. For this reason the discussion of solvent functions will be confined to the sections dealing with lacquers.

LACQUERS

1409. A lacquer-type coating may be extremely simple, consisting only of a film-forming resin and a volatile solvent, *e.g.*, floor shellac, which contains shellac dissolved in denatured alcohol. However, the great majority of lacquer-type coatings are based on cellulose nitrate, ethyl cellulose, or to a lesser extent other polymers, which act as binder. In addition, they contain resin, permanent external plasticizer, solvents, and

TABLE 14-3. TYPICAL LACQUER MIXES

Ingredient	% by Wt
Clear wood lacquer:*	
Cellulose nitrate, $\frac{1}{2}$ sec (dry basis).....	13
Ester gum.....	44
Toluene.....	15
Ethanol.....	7
Butanol.....	8
Ethyl acetate.....	13
Total.....	100
Gloss brass-polishing lacquer:	
Cellulose nitrate, 15 to 20 sec (dry basis).....	8
Modified maleic alkyd resin (hard type).....	6.5
Dibutyl phthalate.....	3.5
Ethyl acetate.....	20
Butyl acetate.....	12
Butanol.....	12
Toluene.....	38
Total.....	100
Automobile lacquer:†	
Cellulose nitrate, $\frac{1}{2}$ sec (dry basis).....	13
Modified alkyd resins (dry basis) ..	4.5
Plasticizer.....	3.5
Alcohols.....	13
Acetates.....	49
Hydrocarbons.....	17
Total.....	100

* Applied by dipping or may be sprayed after reduction with 4 volumes of thinner.

† Use paste colors with above in the proportion of $1\frac{1}{2}$ lb to the gallon.

diluents. Color and pigment may or may not be added. Since the drying of a lacquer does not involve chemical reactions, catalysts are not required. A few typical lacquer mixes are shown in Table 14-3.

1410. Lacquer Resins. Resins are added to lacquers for several reasons. They often improve adhesion. (Cellulose nitrate itself does not adhere well to many surfaces.) Hard resins enhance gloss and hardness and often increase the durability and wearing properties of the film. The combination of cellulosic-derivative binder and resin is better than either alone. Furthermore, resins increase the total solids content of the lacquer mix without appreciably increasing its viscosity since the molecules are not very large. Hence, coatings of suitable thickness and substance are more easily attained. Finally, they often enhance resistance to weather, light, or moisture.

Dammar and other natural resins, ester gum, and glycol esters of rosin are widely employed. Modified phthalic and maleic resins are enjoying an ever-wider application at the current writing. They plasticize cellulose nitrate and have the advantage over plasticizers of lower molecular weight that they are not lost by slow evaporation.

1411. Lacquer Plasticizers. External plasticizers employed in lacquers are of two general types. The *solvent type*, including dibutyl phthalate, tricresyl phosphate, triphenyl phosphate, and camphor, forms uniform dispersions or solid solutions. There is complete miscibility with the binder. Such plasticizers yield films that tend to stiffen and embrittle at low temperatures. The *nonsolvent type* includes raw and blown castor, blown soybean, specially treated linseed and tung, and other nondrying oils and exhibits only limited miscibility with the binder. The films may be considered to be two-phase systems containing plasticizer-rich regions held by surface forces in a network of plasticizer-poor material. Films so plasticized exhibit better low-temperature flexibility. The coatings applied to base fabrics in the manufacture of artificial leather are of this type. When used alone, the nonsolvent type of plasticizers show an exaggerated tendency to sweat or bleed out of the film. Best results are obtained by using a mixture of solvent and nonsolvent types of plasticizers, for example, 1 part of raw castor oil, 2 parts of tricresyl phosphate.

1412. Lacquer Binders. Modern lacquers may be said to have had their commercial start on a large scale in 1923 when cellulose nitrate lacquers were first used in this country for coating automobiles. These coatings were sprayed. To be successful the solution viscosity had to be kept below 70 centipoises while the cellulose nitrate concentration was being maintained at 10 per cent or more. The cellulose nitrates made up to that time were produced for plastics applications (Table 4-8, page 139). Their average D.P. was around 500 to 600, and their solution

viscosities were very high even at low concentrations. They were not suited for lacquer work since not enough could be dissolved in solutions of a viscosity suitable for spraying to yield a surface coating of reasonable thickness except through the very expensive procedure of applying a great number of successive coats.

Obviously the solution viscosity may be lowered by decreasing the average D.P. of the binder. However, this is accompanied by loss of strength and film-forming properties, the mechanical properties dropping off sharply at a D.P. of around 100 or more. It was not until a successful commercial process for manufacturing uniform-quality cellulose nitrates of a D.P. of around 175 was developed that commercially feasible spray lacquers could be made.

Although at the current writing cellulose nitrate is still by far the most widely employed lacquer binder, others, notably ethyl cellulose, cellulose acetate-butyrate, and other cellulosic derivatives, are enjoying increasing application.

1413. Lacquer Solvents and Diluents. As indicated previously, one of the most urgent problems in the lacquer field is to produce a product of a viscosity low enough for spraying or brushing and yet of such a high solids content that an effectively thick film can be attained with few coats. Otherwise, costs are too high. A variety of techniques may be employed to gain this objective, as follows: (1) the use of low-viscosity (low-molecular-weight) binders; (2) the use of large percentages of (low-molecular-weight) resins; (3) hot spraying; (4) improved spraying equipment capable of handling more viscous materials; (5) the use of vehicles of high solvent power. All these techniques are being constantly exploited and improved. All have limitations.

The interrelationships among viscosity, solubility, and gelation were discussed in Secs. 314 to 316. Since it was shown that the solvent having the greatest solvent power also yields the solution of lowest viscosity, it will be understood why excellent solvents are an absolute necessity in lacquer-type coatings.

Lacquer-solvent power may be evaluated by the determination of solution viscosities and dilution ratios, toluene being the usual "non-solvent" for the latter determination (Sec. 315). A typical example of the effect of solvents on the viscosity-concentration curve of a lacquer binder is shown in Fig. 14-1. For reasons advanced in Secs. 309 and 314-316, cellulose nitrate and other common lacquer binders are more soluble in properly chosen mixed solvents than in single solvents.

The solvents employed with lacquers are divided into three categories.

1. *Active solvents.* These are characterized by their ability per se to produce solutions of low viscosity and high binder concentration that dry to films free of defects such as pinholes, waviness, or "orange peel."

Among them are many esters, ketones, and alcohol ethers such as ethyl acetate, amyl acetate, acetone, isobutyl ketone, and 2-ethoxyethanol (Cellosolve) and other ether derivatives of ethylene glycol.

2. *Latent solvents.* These are mainly alcohols that by themselves are unsatisfactory lacquer solvents but, in the presence of active solvents,

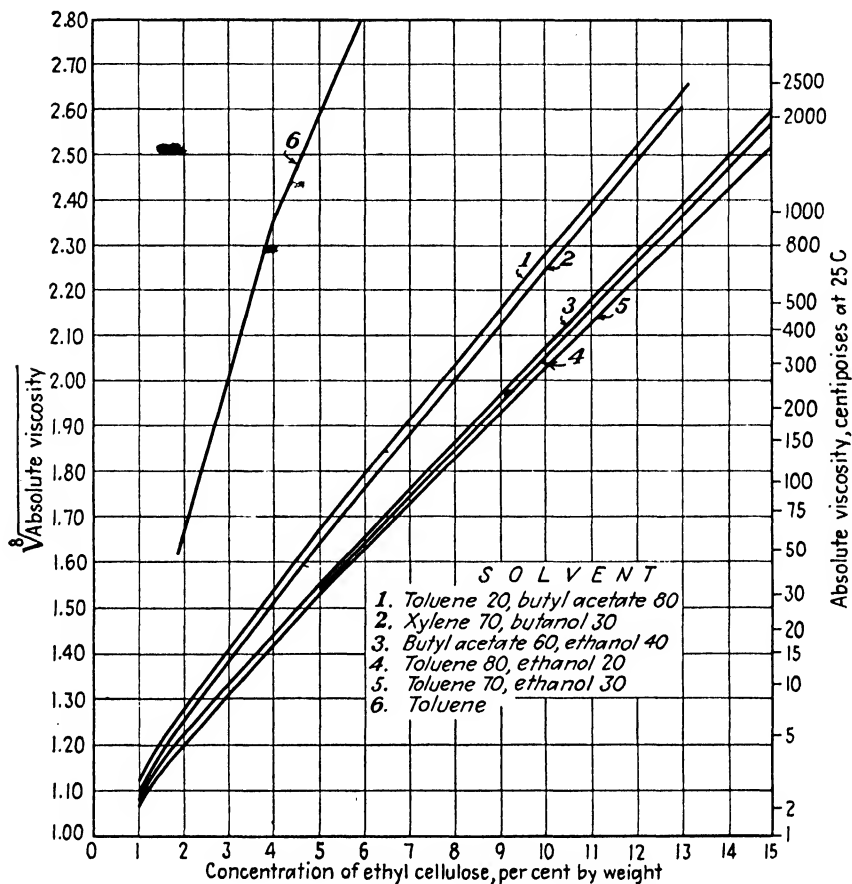


FIG. 14-1. Effect of solvent on viscosity-concentration curves of ethyl cellulose. [T. A. Kauppi and S. L. Bass, *Ind. Eng. Chem.*, **29**, 800 (1937).]

result in enhanced solubility and lower viscosity. Examples are ethyl, isopropyl, isobutyl, butyl, and amyl alcohols.

3. *Diluents.* The diluents are aromatic or aliphatic hydrocarbons. By themselves they are not lacquer solvents. They depend upon the presence of active or latent solvents for compatibility. They are added to thin the lacquer, modify evaporation rates, and reduce solvent costs.

Among them are straight and hydrogenated petroleum naphthas, toluene, and xylene.

It is evident from this discussion that factors other than viscosity and solubility must be considered in formulating a lacquer solvent (Secs. 1420 and 1421). Some commercial combinations are listed in Table 14-4.

Just how effective correct solvent balance can be has been demonstrated in gel lacquers. A *gel lacquer* is one that undergoes reversible gelation in a narrow temperature range without change in solvent content. These coatings are applied by dipping. The composition of the solvent is so adjusted that at the temperature of application (~ 120 F) the lacquer is a smooth, "flowable," viscous liquid. However, when cooled to room temperature without loss of solvent, it sets rapidly to a firm gel. The applied coating does not sag or wrinkle although it shrinks as solvent evaporates *after* application. Many new uses await this type of lacquer since it is possible in one dip to deposit a coating 15 mils thick as compared with the usual 1 or 2 mils.

ADHESION

1414. A surface coating must adhere tenaciously to the object it is to protect. What causes one material to stick to another is a matter of tremendous theoretical and practical importance. This subject is considered in greater detail in Chap. 15.

There are two broad types of adhesion, *mechanical adhesion*, which depends on penetration of a porous surface; and *specific adhesion*, in which molecular forces, either primary or secondary, are brought into play, rather than mechanical anchorage.

1415. Mechanical Adhesion. When porous, penetrable surfaces such as those of wood or cloth are involved, mechanical adhesion may be of importance. For example, if a varnish-type coating is applied, the vehicle penetrates the surface, solvent evaporates, and the binder polymerizes, resulting in mechanical anchorage (as well as specific adhesion) to the surface. It is found that the adhesion of paints to wood increases with the degree of penetration, a common consequence of insufficient penetration being peeling and blistering.

Mechanical adhesion is, of course, influenced by the porosity of the substrate. Balsa is an extremely open wood; maple is comparatively dense (Fig. 9-24, page 397). End wood is always highly penetrable. The moisture content of the wood is also a factor. A vehicle that penetrates deeply into dry wood will show poor penetration if the same wood is wet. The pigment content of the paint likewise plays a part, penetration decreasing as the amount of pigment increases. A good priming coat must not be too heavily loaded with pigment.

On ultraporous surfaces, penetration may be too extensive to be com-

patible with economy. Sealing coats may be applied in such cases; or the vehicle may be specially designed so that gelation occurs as soon as the volatile components of the mix begin to evaporate. This is usually accomplished by incorporating special metallic soaps or rapidly gelling oxidized or sulfurized oils.

1416. Specific Adhesion. Adhesion due to molecular forces is most directly observable on smooth, impenetrable surfaces such as those of glass and polished metal, where mechanical adhesion is obviously unimportant. There are always unbalanced forces at a surface that render it more active than the interior of the mass (Sec. 216). Specific adhesion involves the intermolecular forces at the interface between the surface coating and the substrate.

It is a generalization of notable importance that surface coatings containing polar constituents such as carboxyl and hydroxyl compounds usually exhibit better general adhesion to wood and metal than those not containing such constituents. Phenol-aldehyde resins are relatively non-polar and often show poor adhesion under the same conditions where urea-aldehydes, which contain more polar structures, will give surface coatings that adhere much better. Surface-coating adhesion is often improved by the deliberate introduction of substances containing active polar groups.

From the behavior of many systems it appears that, if two surfaces are to be joined which are quite different in polarity or chemical nature, adhesion is fostered by the introduction of an interlayer having groups or molecules so oriented that one side of the interlayer adheres to one surface and the other side adheres to the second surface. For example, an organic surface coating may not adhere well to iron. If, however, the latter is treated with a phosphate solution, a surface layer of iron phosphate forms and strong adhesion results. Presumably there is an orientation of the two-dimensional iron phosphate layer, with the phosphate groups oriented outwardly from the metal. The phosphate structure is compatible with the organic surface coating, and good adhesion results. Similarly, the treatment of galvanized (zinc-coated) iron with chromic acid results in good adhesion to organic surface coatings. Presumably an oriented zinc chromate layer is formed in which the zinc end of the molecule adheres to the metal and the chromate group adheres to (is compatible with) the surface coating. The zinc chromate need not be formed by chromic acid treatment of the metal surface. It may be added as such to a primer coat, which, when applied to metals, results in good adhesion of the final coating. Paints sometimes adhere to tarnished metal surfaces better than to bright metals because the corrosion compounds on the surface (oxides, carbonates, sulfates, sulfides,

etc.) are more compatible with the paint than the metal itself. Rusted iron is an exception for the simple reason that ordinary iron rust adheres poorly to the metal. If, however, the iron surface is uniformly oxidized by subjection to high temperatures or the application of a red-lead primer, adhesion is excellent. Finally it must be pointed out that in some metal-paint systems, good adhesion is not obtained unless the coating is baked on at elevated temperatures, indicating that chemical reaction leads to the formation of a two-dimensional binding interlayer, which is a necessary concomitant to good adhesion.

It follows from the above discussion that the adhesion of a coating depends upon the nature and the condition of the base. The preparation of the surface of the base is of the utmost importance. It is a frequently repeated statement that "a paint can be no better than the surface to which it is applied." Gloss as well as adhesion is very directly dependent upon the care with which the surface has been prepared, and it is probably safe to state that more jobs are ruined by dirty, moist, or poorly prepared surfaces than by poor surface-coating materials. Proper conditioning of the base is important in gluing operations for much the same reasons.

Although mechanical and specific adhesion have been discussed separately, it must not be forgotten that in many cases they may be simultaneously involved.

1417. Forces Working against Adhesion. From the time a surface coating has been applied, there are forces constantly at work to detach the film from its base. Owing to differences in the expansions and contractions of surface coatings and their bases (Table 10-4), fluctuations in temperature tend to detach the coatings or cause them to crack. Changes in humidity may act similarly if the amounts of swelling due to moisture absorption are different in the coating and base, as is particularly true for wood.

Many surface coatings shrink slowly on aging. In varnish-type films this may be due to slow, progressive polymerization or loss of retained solvent. In lacquers it is often traceable to gradual loss of external plasticizers as well as solvents. In either case this is another factor tending to loosen the coating from its anchorage.

Highly flexible films with rubbery characteristics, such as long-oil varnishes and rubber-plastic combination adhesives, can accommodate themselves so well to dimensional changes that the forces discussed above do not develop sufficient stresses to cause checking or detachment. By contrast, lacquer-type coatings and rigid films in general are particularly sensitive to them, especially when applied to iron and brass.

Surface coatings exhibit wide differences in their permeability to gases and vapors. Glyptal resins are relatively dense and impervious. Oleo-

resinous films, particularly those long in oil, have a dendritic space-polymerized structure that, by contrast, is wide open. Permeability, especially to water vapor, plays an important role in adhesion. A very dense film that cannot "breathe" tends to peel when water vapor forms beneath it. This effect is most likely to manifest itself in surface coatings applied to wood since wood undergoes extensive changes in moisture content with variations in temperature and humidity. A certain modicum of permeability is vital for wood coatings. On the other hand, if a film applied to iron is highly permeable to water vapor, it will not protect the iron from rusting and the latter will eventually weaken adhesion.

DRYING RATES

1418. The ability to dry rapidly is one of the most valuable assets a surface coating can possess. One has only to consider the difference in convenience in a home when a floor coating requires only a few hours rather than overnight to dry. Rapid drying means rapid production schedules in factories, coupled with a small investment for drying space and equipment. Rapid drying also tends to result in "dust-free" drying.

The cellulose nitrate lacquers were developed in response to an insistent demand for durable automobile-body finishes that would dry rapidly and thus eliminate a bottleneck on the production line. Indeed, the greatest inherent advantage of lacquers over varnishes is quick drying at ordinary temperatures. A lacquer will often be dry to touch in a few minutes and will dry hard in 1 to 6 hr at room temperature. By contrast, varnishes require anywhere from 4 to 36 hr. The large-scale introduction of lacquers in 1923 started a competition and a struggle for improved drying rates that has never ceased.

1419. Drying of Varnishes. The drying of oleoresinous varnish films is catalyzed by the incorporation of driers. There is a limit to which this can be carried. Too much drier results in an overoxidized, "burned" film, which wrinkles and manifests poor chemical resistance. This leads to rapid aging and deterioration. A better way to produce quick-drying varnishes is to incorporate synthetic phenolic resins (Secs. 1618 and 1619). These accelerate polymerization, not oxidation, and yield films that not only dry rapidly but also possess outstanding durability. The so-called "four-hour enamels" are phenolic-resin varnishes developed to compete with lacquers.

Another method for speeding the drying of all types of varnishes is the use of infrared lamps. The heat rays are absorbed by the surface coating itself. It is not necessary to through-heat the entire object, a time-consuming and expensive procedure. Tunnels studded with infra-

red lamps have made it possible to bake varnish-type coatings on automobiles at an amazing rate.

1420. Drying of Lacquers. The drying rate of a lacquer depends almost solely on the volatility of the solvents and can be varied over wide limits by changing the solvent composition. It is possible to formulate lacquers that may be buffed within less than 2 min after application. On the other hand, lacquers that are to be hot-sprayed require solvents of lesser volatility. But whether a lacquer is to be quick- or slow-drying, it is essential to use solvent mixtures that deposit the film in such a manner that pinholing, waviness, and other surface defects are avoided. Three typical solvent combinations used for wood lacquers are shown in Table 14-4.

TABLE 14-4. LACQUER-SOLVENT COMBINATIONS

Quick-drying		Medium-drying		Slow-drying	
Item	% by volume	Item	% by volume	Item	% by volume
Toluene.....	50	Toluene.....	60	Xylene.....	30
Isobutyl acetate....	15	Butyl acetate.....	30	Petroleum naphtha	20
Ethanol.....	15	Butanol.....	10	(240-290 F)	
Methylethyl ketone..	10			Butyl propionate...	20
Isopropyl acetate...	5			Butanol.....	15
Secondary amyl acetate.....	5			Amyl alcohol.....	10
				Ethyl lactate.....	5

GLOSS AND GLOSS RETENTION

1421. The original gloss of a surface coating is influenced by several factors (Secs. 1017 and 1018). The addition of pigment beyond a certain maximum value destroys the smoothness of the surface and reduces gloss. Improper kettling or compounding or, in fact, anything that causes drying to a wrinkled film will impair gloss. In varnishes, the incorporation of too much drier may lead to the formation of a rapidly polymerized superficial skin, which prevents drying of the inner body of the film. Wrinkling, with attendant loss in gloss and durability, follows. Wrinkling also results when an uneven coat or too thick a coat is applied.

If a pigmented film dries in such a manner that a layer of clear vehicle forms at the surface, a film of high gloss results. The refractive index of the resin or resin-oil components of the mix is also a factor. For example, it has been found that increasing the refractive index of a clear varnish resin-oil mixture from 1.4 to 1.5 increases the gloss, as measured by the

amount of reflected light, by about 50 per cent [Eq. (10-18), page 459]. Poorly balanced solvent mixtures in lacquers may cause irregularities in the film surface. Vortex currents set up during evaporation can cause the surface defect known as *orange peel*. The development of turbidity in lacquer films is known as *blushing*. Blushing tendencies in cellulose nitrate lacquers are minimized by avoiding free glycerol and resins with acid numbers above 20. Glycerol is hygroscopic and causes blushing by absorbing moisture. Lacquers will also tend to blush when dried at temperatures too close to the dew point. Humidity control in lacquer rooms is usually necessary.

The above factors control the original gloss. The main factor causing loss of gloss subsequent to application of the coating is deterioration of the surface of the film by oxidation or hydrolysis. Gloss *retention* is therefore intimately associated with the chemical character of the film constituents.

There is a tendency, particularly in moist climates, for oleoresinous varnish films to develop a bluish, hazelike discoloration when exposed to drafts. This discoloration is known as *bloom*. To the varnish manufacturer it is a troublesome phenomenon, and its avoidance must always be considered in formulating the mix. Just what it is has not been established, but considerable information is available on what induces or suppresses it. Thus, the following tend to induce bloom: cobalt and (to a lesser extent) lead driers, tung oil, free abietic acid, and rosin compounds in general. On the other hand, the presence of manganese driers, calcium salts, linseed oil, and phthalic and phenolic resins tends to suppress it.

MECHANICAL PROPERTIES OF DETACHED SURFACE-COATING FILMS

1422. Measurements made on stripped, detached, unanchored films may afford a valuable insight into surface-coating problems. From the discussion of adhesion, it will be understood why a good surface-coating film must possess a modicum of flexibility, extensibility, and toughness if it is to remain anchored. It should possess some degree of rubberiness. The most informative measurements that can be made on detached films are those of tensile strength and elongation at break. The former should be calculated from the actual cross section at the moment of rupture. Organic surface coatings are sufficiently similar mechanically to permit these two measurements alone to serve as a basis for deducing other important properties and evaluating the relative merits of the coatings in general. For example, high extensibility is always accompanied by high flexibility, and high tensile strength may be taken as a reliable indication that the abrasion resistance will be good. Toughness is, of course, directly calculable from the two original measurements, and high tough-

ness is accompanied by high impact strength. On this basis, organic surface-coating films may be divided into four categories as follows:

1. *High tensile strength and high extensibility* represent the ideal combination. They indicate a film that is simultaneously strong, tough, and flexible. Such a film will tend to resist breakdown from alternate expansion and contraction and will withstand abrasion and impact. This combination of properties is often exhibited by properly formulated nitrocellulose and ethyl cellulose lacquers, alkyd-resin coatings, and tung oil-phenolic resin varnishes.

2. *Low tensile strength and high extensibility* signify a film that is soft and plastic and highly flexible. Such a film is applicable where flexibility and resistance to cracking are more important than hardness and abrasion resistance. Varnishes long in oil are an example of this type.

3. *High tensile strength and low extensibility* characterize a film that is hard and resistant to abrasion. Although not necessarily brittle, a film of this type is usually not well suited to resist alternate expansions and contractions over wide temperature limits, for it will tend to crack. Oleoresinous varnishes of medium oil length fall into this category.

4. *Low tensile strength coupled with low extensibility* indicates an organic surface coating that is hard, brittle, and weak. It will be likely to have a short life, being unable to withstand impact, aging, or alternate expansion and contraction.

For surface coatings that must withstand low or high temperatures or wide ranges of temperature the temperature coefficient of flexibility should also be determined. The lowest temperature to which a coating will maintain flexibility depends upon the brittle points of the high-polymer constituents (Sec. 519) as well as the amounts and types of plasticizer present. Cold flexibility is of particular significance in coatings for aircraft and refrigerator equipment as well as in making artificial leathers. Ethyl cellulose coatings exhibit outstanding merit in this regard.

FLAWS, WRINKLES, AND CRACKS

1423. A surface-coating film breaks down by cracking. If at any point in the film, a tension is set up exceeding the tensile strength of the film at that point, the film parts. By microscope examination repeated at intervals, it is found that every film breakdown starts at mechanical weak spots. These weak spots may be pinholes, blisters, scratches, wrinkles, or minute pores caused by local chemical action, occluded air, grit, or insufficiently wetted pigment particles.

The mechanism of breakdown is best observed in transparent coatings. The unstressed coating is optically homogeneous, but if subjected to

stress it becomes doubly refractive. If a coating that has developed cracks is examined under a microscope with polarized light, it is found that regions of high internal stress surround the cracks. By similar examination it is found that, if a film is subjected to tension, stresses develop around any pore or pinhole at right angles to the direction of the applied tension. If the latter grows too great, a crack starts.

The tensions that result in breakdown may be caused by external forces such as warping or bending of the base or nonuniform expansion and contraction of the coating and base with changes in temperature or humidity. Or they may be developed internally by crystallization of film constituents, wrinkle formation, or film shrinkage due to aging.

The inherent advantages of complex surface-coating molecules of poor symmetry are obvious. They exhibit little tendency to crystallize and possess sufficient inherent extensibility to remain essentially unstressed during the normal elongations accompanying thermal or other expansions.

The formation of a wrinkle for whatever reason is evidence *ipso facto* of a region of stress. A film wrinkle is the invariable forerunner of a crack. Cobalt driers produce deep wrinkles with strong cracking tendencies. Manganese and lead driers yield shallow wrinkles with lesser breaking tendencies. As previously mentioned, wrinkles also may be formed during the shrinkage accompanying film aging. In other cases they are coincident with chemical changes occurring in the film.

Chemical breakdown may be initiated from without by reactions between the components of the atmosphere and those of the film; or they may start from within, as, for example, when pigment (alkaline) reacts with the acid groups of resins or free fatty acids to form heavy metal soaps. In either case the reactions may eventually result in weak spots, unequal tensions, and breakdown.

Just as the adhesion of a surface coating is vitally dependent upon proper preparation of the surface to which it is applied, so also are its performance and durability influenced by the manner in which it is applied. For every surface coating there is a film thickness that results in optimum durability and mechanical properties. Thicknesses greater or less than this optimum decrease the service life. The same coating at two different film thicknesses may exhibit entirely different types of failure. This factor is particularly noticeable in brushed varnish types of coating. Even when such coatings are applied by a skilled workman, variations in coating thickness may be detected. In the hands of a tyro or careless worker, the irregularities may be so great that the performance of the coating is drastically reduced. If the coating is applied too thinly, weakness and rapid breakdown usually follow, whereas too thick a film results in wrinkling and other surface defects.

PIGMENTS

1424. By contrast with clear varnishes and lacquers, paints and enamels contain pigments in the form of dispersed, finely ground solids. They are most often present as major constituents and act simultaneously as coloring materials and fillers in the final surface-coating film. They may increase or decrease the life of a coating, depending upon whether they have been properly or improperly chosen and whether or not they are present in the correct amounts.

1425. Reactions between Pigment and Vehicle. Some of the more important paint pigments are nonreactive; others, such as oxides of iron, lead, and zinc, white lead, and whiting, are alkaline in character. Since the vehicles of many surface coatings contain acidic ingredients, chemical reactions between them and alkaline pigments often take place, with the resultant formation of heavy metal soaps or similar compounds. As previously pointed out, excessive soap formation may cause rapid deterioration in paint films. Since varnish-type coatings contain more generally reactive binders than lacquer types, it is obvious that chemical reactions are more extensive and more generally significant in the former than in the latter.

However, regardless of the type of coating and pigment, the particles of the latter are so fine and are possessed of such an enormous surface that the interfacial forces acting between pigment and vehicle almost invariably produce effects of considerable consequence in the surface-coating mix as well as in the ultimate film. Several of these effects are discussed below. It should be borne in mind that much of what is said about paints applies likewise to pigmented inks.

Through exposure tests it has been well established that the life of exterior house paints is longer with properly selected combinations of pigments and extenders than when any one pigment is used alone.

1426. The Wetting and Dispersion of Pigment Particles. If a surface-coating mix is to be of good grade, it is absolutely essential that the pigment particles be properly wetted by the liquid medium. Unless thorough wetting is effected, inordinate settling and caking may occur in the container or weak spots may form in the paint film (Sec. 1423).

Modern pigments are of very small ultimate particle size. The object of present-day paint grinding is not so often to fracture the particles as to break up, or deflocculate, agglomerates of the ultimate particles and disperse the latter. In the conventional paint-grinding mill, this is accomplished by the pressure and friction exerted by hard surfaces. In the disperser type of mixer, on the other hand, it is brought about by the shearing forces set up in a viscous vehicle, and it is generally

true that the dispersing action increases with increase in the viscosity of the grinding vehicle. Roller-mill grinding combines the effects of friction of hard surfaces and the action of the shearing forces of viscous vehicles.

Owing to surface forces, dry pigment particles are often covered with a very thin envelope of tightly bound air, which must be removed during grinding if wetting by the vehicle is to take place. In other cases, extremely tenacious moisture films may be found, which cannot be completely eliminated by ordinary grinding. These may cause trouble by inducing hydrolysis of the vehicle at the pigment-vehicle interface during the grinding operation.

Difficulties arising from both air and moisture envelopes may often be eliminated by pretreating the pigment with sufficient of a suitable wetting agent to form its own monomolecular adsorbed layer over the particles. This satisfies the surface forces and prevents the formation of the troublesome air and water films. For example, the pigment (especially one of alkaline reaction) is treated with a dilute solution of fatty acid and the volatile solvent subsequently evaporated. A very stable film of oriented fatty acid molecules surrounds the particles, with the carboxyl groups directed toward the pigment and the paraffinic chain portions pointed outward. This oriented layer not only acts as lubricant, preventing particles from agglomerating, but also renders them readily wettable by organic solvents and vehicles. The dispersing efficiency increases with the chain length of the fatty acid, reaching a maximum with the 14-carbon-atom (lauric) acid. Polymerized drying oils, aluminum stearate, zinc soaps, barium resinate, and similar compounds are also used.

An interesting side light to this behavior presents itself. A serious decrease or even complete loss of drying properties is occasionally observed in paints and enamels containing certain combinations of pigments and driers. It will be recalled that the latter are mainly soaplike compounds of cobalt, manganese, and lead. The evidence is that in some cases the loss of drying ability is attributable to the adsorption of drier by the pigment and may be prevented by pretreatment of the latter with an appropriate surface agent.

Another important point is that, if a pigment is successively exposed to different substances capable of wetting it, the first material adsorbed is often held tenaciously and is not replaced by the materials subsequently added. This explains why occasionally the sequence of addition of ingredients may considerably affect the quality of the final product.

By varying the pretreatment, one and the same pigment may be rendered dispersible in either organic solvents or aqueous media. Water paints (Secs. 1441 *ff.*) naturally require water-dispersible pigments.

Dispersibility may also be attained by treating pigments with appropriate protective colloids. Caking and settling may sometimes be prevented by adding an ingredient that forms a thixotropic gel in the mix.

1427. Effects of Pigment on Flow Properties. The flow characteristics of a paint are of first importance. As explained in Sec. 719, it should be thixotropic in accordance with the following criteria: The thixotropic set should impart sufficient body during storage to minimize settling of the pigment. However, the paint should readily become fluid under the brush but set again, after brushing ceases, at a rate such that

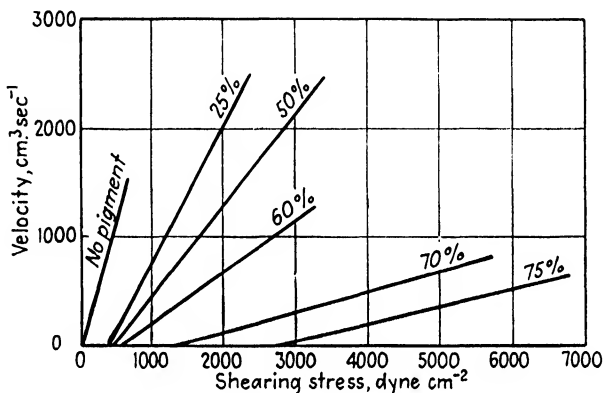


FIG. 14-2. Effect of lithopone on viscosity and yield value of a linseed-oil paint. (R. Houwink, "Elasticity, Plasticity, and Structure of Matter," 1940. By permission of the Macmillan Company, publishers, and Cambridge University Press.)

brush marks have sufficient time to level out. Increased concentration of suspended particles increases the consistency and the yield point (Sec. 624). A series of flow curves for a lithopone-linseed-oil paint is shown in Fig. 14-2. The oil alone is a Newtonian liquid; but as lithopone is dispersed, increasing yield values develop. Both the size and the shape of the dispersed particles affect the rheological properties. Plate- and rod-shaped and flocculated particles impart yield values at relatively low concentrations. Similar flow characteristics and thixotropy may be induced in emulsion-type surface coatings, the fine droplets of the emulsion playing a role similar to that of solid pigment particles.

Livering, a common trouble in paints and printing inks, is the development of an inordinately high yield value and consistency upon aging of the mix. The livered mass is a stiff, irreversible gel, which will not brush out or flow. Livering tendencies are most pronounced in paints containing chemically active pigments such as red lead and zinc oxide, and both the kind and the amount of acidity in the vehicle have important effects; high concentrations of free rosin or fatty acids are deleterious.

Surface reactivity and pigment particle size are important determinants of the rate of livering.

From the above it is evident that paints can be overground. In some cases, only a limited breakdown of agglomerates is required to attain the particle size that creates the most suitable thixotropic properties. In other cases, too much grinding may render otherwise inert pigments so reactive that livering results.

1428. Pigments and Optical Properties. The *hiding power*, or opacity, of a paint film depends upon how much of the incident light is reflected or absorbed before reaching the protected surface. If no light reaches the latter, it is perfectly obscured. In practice, the hiding power of surface coatings is often measured by applying them to a surface of contrasting black and white or gray and white patches. It is usually reported in square feet (hidden) per gallon. It is influenced by film thickness, pigment concentration, and other such more or less obvious factors, which will not be discussed. Instead, attention will be centered on the pigment properties of more fundamental significance.

Dark pigments have great hiding power merely because they absorb a large portion of the incident light. However, colorless materials also exhibit hiding power when reduced to small particle size owing to the scattering of light by reflection and refraction. The amount of this scattering increases with (1) the fineness of the particles and (2) their refractive index (Secs. 1017 and 1018). White pigments differ considerably in refractive index (Table 14-5). Those of high index yield opaque films

TABLE 14-5. APPROXIMATE REFRACTIVE INDEXES OF SOME WHITE PIGMENTS

Pigment	Refractive Index
Titanium dioxide.....	2.5
Zirconium oxide.....	2.4
Zinc sulfide.....	2.4
Antimony oxide.....	2.2
Zinc oxide.....	2.01
Basic carbonate white lead.....	2.00
Basic sulfate white lead.....	1.9
Barytes.....	1.64
Calcium sulfate.....	1.6
Calcium carbonate (chalk).....	1.6
Talc.....	1.57
China clay.....	1.56
Silica (quartz).....	1.55
Diatomaceous earth.....	1.43

[Eq. (10-17)] and are termed *strong pigments*, while those of low index lack hiding power and are known as *extenders*. The refractive indexes of practically all surface-coating oils and resins are 1.57 ± 0.10 .

Although pigments and vehicles manifest a certain degree of inherent difference in their abilities to form glossy films, the most important

determinants of gloss in pigmented coatings are the volume ratio of pigment to binder and the state of dispersion of the pigment. High pigment binder ratios (Table 14-7) and poor dispersion reduce gloss.

Diffusely reflected light is ideal for reading and working. Hence, flat paints are more desirable for most interior wall surfaces than gloss paints. Owing to the absorption of certain wave lengths, the lightness of colored paints cannot, of course, be as high as that of a good white paint. Among white pigments there is a close correlation between refractive index, particle size, and lightness.

1429. The Effects of Pigment Concentration. At various points in this chapter it has already been indicated how the pigment concentration influences adhesion, durability, flow characteristics, hiding power, and gloss. This factor is so important that it is a major determinant of the *type* of surface coating. Representative weight and volume compositions of several leading types of oleoresinous paints are presented in TABLE 14-6. REPRESENTATIVE COMPOSITIONS OF SEVERAL TYPES OF OLEORESINOUS PAINT AND ENAMEL

Component	Flat wall paint		Exterior house paint		Interior enamel	
	Wt %	Vol %	Wt %	Vol %	Wt %	Vol %
Vehicle (binder); drying oils, resins, and driers.....	15	25	27 (no resins)	62.5	30	45
Pigments.....	62	25	68	25	50	15
Volatile solvents.....	23	50	5	12.5	20	40
	100	100	100	100	100	100
Pigment-binder ratio.....	...	1.0	...	0.4	...	0.33

TABLE 14-7. PIGMENT-BINDER VOLUME RATIO AND OLEORESINOUS-PAINT CHARACTERISTICS

Pigment-Binder Volume Ratio	Paint
2.5.....	Flat paint. Poor durability and adhesion
1.0.....	Flat to eggshell paint
0.8.....	Gloss paint
0.5 to 0.33.....	House paint
0.33 or less.....	Enamel
0.0.....	Clear varnish

Table 14-6. Table 14-7 contains a rough correlation between oleoresinous-paint characteristics and pigment-binder volume ratios. (Volume ratios are more significant than weight ratios.)

Because they contain binders in fully polymerized form and hence of high viscosity and low solubility, lacquer-type coatings are generally leaner in film-forming constituents than varnish types. Whereas an

average oleoresinous paint might contain 6 to 8 lb of pigment per gallon, a like amount in a lacquer coating would result in a film devoid of adhesion and durability. For lacquers, pigments of high opacity and low binder absorption are generally required, serving to keep the pigment concentration low and at the same time protecting the binder, particularly cellulose nitrate, from the rapid decomposition and discoloration caused by the actinic rays of sunlight.

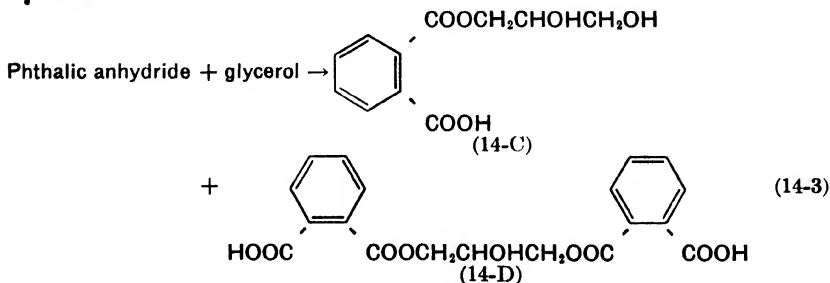
THE SERVICE LIFE OF SURFACE COATINGS

1430. The life of a surface coating depends upon proper formulation of the mix, the preparation of the surface, the method and care of application, the conditions extant during drying, and the chemical, climatic, and mechanical environment, as well as its own adhesion, mechanical properties, and chemical composition. No attempt has been made to cover all aspects of the subject. Detailed treatments are found in the texts and periodicals devoted to the field.

POLYESTER (ALKYD) SURFACE-COATING RESINS

1431. At the current writing the most important applications of synthetic polyesters lie in the field of surface coatings. These resins are also known as *alkyd resins*. They are synthesized mainly by reacting polyfunctional combinations of alcohols and organic acids, with or without fatty acids, oils, or modifying resins. The alcohols most commonly employed are glycerol, ethylene glycol, dipentaerythritol, pentaerythritol, and sorbitol; the more usual acids are phthalic and maleic anhydrides and sebacic acid, plus various saturated and unsaturated monocarboxylic acids and resins used as blocking and modifying agents.

1432. Glycerol-Phthalic Anhydride Resins. These resins constitute a major portion of all synthetic-polyester production. Glycerol and phthalic anhydride represent a tri-bifunctional combination. At 200 C, the first carboxyl group esterifies readily with primary alcohol groups of the glycerol to form multifunctional resinoids as follows:



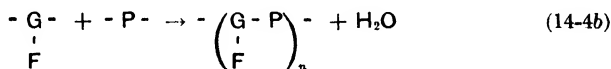
Since the resinoids are multifunctional, they are capable of forming either chain or space polymers, depending upon reaction conditions. The

benzene rings represent kinks on the main chains, producing considerable internal plasticization and lowering the crystallizing tendencies (Sec. 1423).

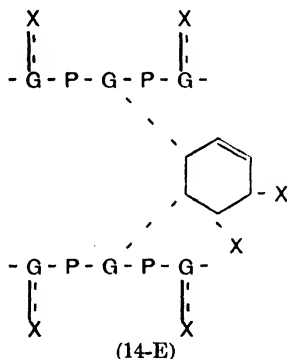
The danger of premature cross-linkage and gelation may be minimized and a further internal plasticization simultaneously accomplished by first blocking one alcohol group of the glycerol with a monocarboxylic fatty acid, thus reducing it to bifunctionality.



Then

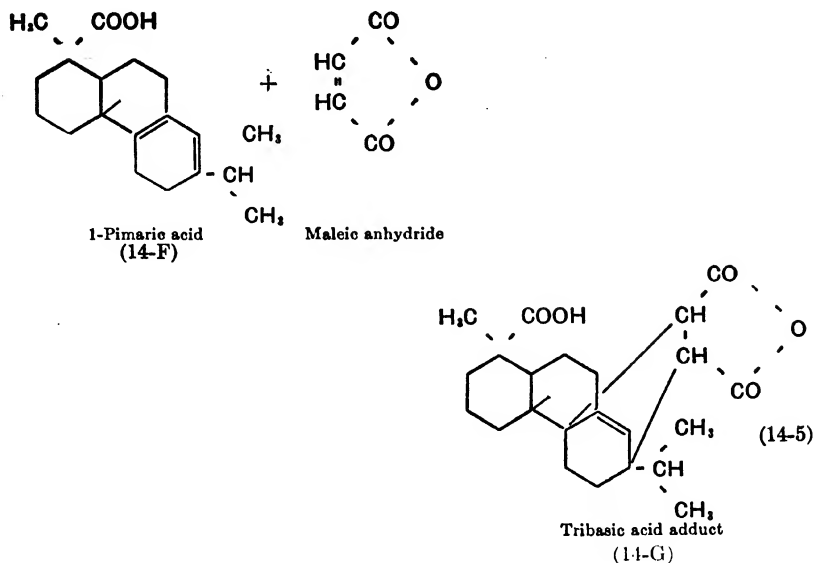


Since 18-carbon-atom fatty acids are commonly employed, the internal plasticization is potent. If the fatty acid is nondrying, the resulting chain-type resins are nondrying. If, on the other hand, drying fatty acids are used, cross-linkage will take place upon baking or air drying; *i.e.*, the resins will be of the drying type. Reaction (14-1) is prominent in the drying process, the final coating containing structures representable by structure (14-E).



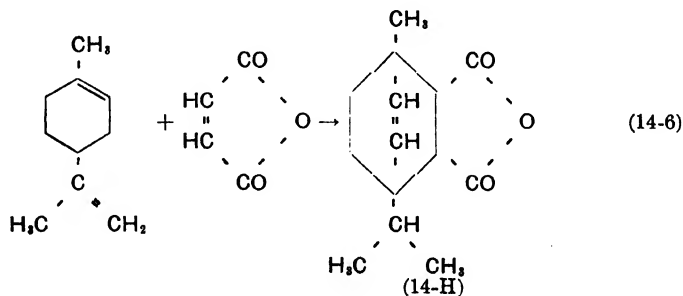
Although the above drying-type resins may be made with drying-oil acids, in many cases they are manufactured from drying oils themselves. Glycerol is cooked with the drying oil in the presence of metallic soaps at temperatures just high enough to promote ester interchange. Mono- and diglycerides are present in the resulting mixture, which is then condensed with phthalic anhydride or other bifunctional acid to form the final resins. Hard resins may be produced by using natural resins as the monocarboxylic blocking agent.

1433. Maleic Resins. When rosin is heated with maleic anhydride, abietic acid [structure (14-B), page 600] first isomerizes to 1-pimaric acid, which then undergoes the Diels-Alder reaction with maleic anhydride to form a tribasic acid adduct.



The resulting trifunctional adduct is used for manufacturing hard resins for varnish-type coatings. If this adduct were condensed with glycerol, itself a trifunctional compound, only two-thirds of the functional groups could condense without gelation occurring (Sec. 406). Hence, in preparing resins of this type, excess rosin is usually added. This *excess* rosin reacts only as a monofunctional carboxylic acid, playing the role of blocking agent. This permits esterification to proceed nearly to completion without gel formation and also serves to control the degree of polymerization, holding the molecules to a reasonable size where their solubility in surface-coating solvents is adequate (Secs. 409 *ff.*).

Dibasic acid adducts suitable for alkyd-resin manufacture may also be made by reacting cyclopentadiene with maleic anhydride. Furthermore, many of the monocyclic terpene hydrocarbons, $C_{10}H_{16}$, although not conjugated dienes originally, undergo rearrangement and subsequent Diels-Alder reaction with maleic anhydride at temperatures above 150 C.

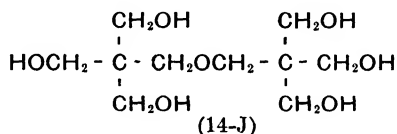


These adducts form alkyd resins that are not as hard as those made from the maleic-rosin adduct. The olefinic bond [structure (14-H)] is reactive and participates in the drying reaction when they are employed in varnish-type coatings.

The copolymerization of polyesters containing carbon-oxygen conjugation with vinyl and other olefin-unsaturated compounds has been discussed in Sec. 433. Resins of this type find applications in the surface-coating field as well as in molding.

1434. Other Polyester Surface-coating Resins. Polyester resins are also produced commercially in which glycols are employed in place of glycerol and linear dibasic acids such as adipic and sebacic are substituted for phthalic or maleic anhydride.

Of more recent development are the polyester resins based on the hexahydric ether-alcohol, dipentaerythritol [structure (14-J)].



This hexafunctional compound affords unique cross-linking potentialities, the fact that its six alcohol groups are all primary being important. Polyester resins made with this substance exhibit greater hardness and water repellency, higher melting point, increased rate of cure, and more rapid drying than the older alkyd resins. Alcohols of lower functionality are ordinarily used with dipentaerythritol to modify the inherent brittleness of the straight dipentaerythritol polyesters.

1435. Applications by Type. The polyester surface-coating resins may be classified into several categories by application and type.

1. *The plasticizing resins.* These resins are almost always of the nonoxidizing kind and are often produced from (a) glycerol, phthalic anhydride, and castor or other nondrying oil or (b) glycerol, sebacic acid, and a nondrying oil. They are used chiefly in lacquers to impart flexibility to other surface-coating polymers. They are supplied commercially as 50 to 80 per cent solutions in butyl acetate, toluene, or xylene. By themselves they do not make very satisfactory surface-coating films, principally because they lack hardness and are relatively slow-drying as lacquers go. However, like other esters they are compatible with a wide variety of resins, which helps to explain their extensive employment as external plasticizers for other resins. Because they are stable and light in color they may be used in clear, white, and pastel-shade coatings. To cellulose nitrate lacquers they impart flexibility, improved stability, and improved adhesion to metals. Special types are used in cellulose acetate coatings. Another important application is in hard baking enamels,

especially in white or pastel colors. These coatings are made from a combination of polyester resin and alcohol-soluble urea or melamine resin (Sec. 1440).

2. *The drying resins.* The drying polyester resins are often made from glycerol and phthalic anhydride plus drying oils or drying-oil acids. Depending on the ratio of glycerol phthalate to fatty acid, a wide range of properties is possible. Those resins high in fatty acid content are soluble in petroleum thinners, but those containing higher amounts of phthalate require aromatic solvents and do not tolerate the addition of substantial quantities of aliphatic thinners. Often these drying polyester resins are used as the entire vehicle for varnish-type coatings much as is linseed or tung oil. Those containing the most unsaturated and most highly conjugated fatty acid constituents dry fastest but show the greatest discoloration (Sec. 1404). When used by themselves as the film-forming polymers, these resins possess many excellent properties but lack hardness. They may be improved in this regard by adding phenol-aldehyde or maleic-rosin resins of suitable compatibility. Still better results are possible by using them in conjunction with alcohol-soluble urea-aldehydes or melamine-aldehydes.

The drying-type resins based on dipentaerythritol also exhibit improved hardness and other advantages cited in the previous section. Their rapid air-drying properties make them particularly attractive for quick-drying varnish-type coatings.

3. *The hard resins.* The hard polyester resins, as the name implies, are used mainly to improve film hardness and gloss. Most of them are based on maleic anhydride. As previously described, the maleic-rosin resins are made by reacting the anhydride with glycerol plus rosin in excess. They are offered in several grades, melting points by the ball-and-ring method varying from 120 to 150 C.

All the hard polyester resins are light in color and are soluble in aromatic hydrocarbons, turpentine, hydrogenated petroleum naphtha, and ethyl acetate. They may be incorporated into both varnish- and lacquer-type coatings where hardness, pale color, and gloss are required.

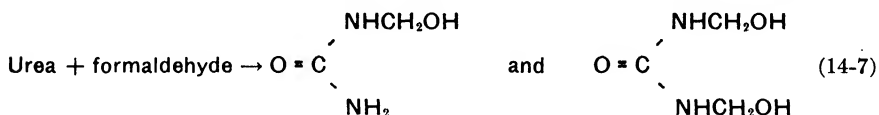
The previously mentioned resins based on dipentaerythritol may be made both as plasticizing and as drying types of a wide range of hardness and compatibility.

UREA-ALDEHYDE AND MELAMINE-ALDEHYDE RESINS

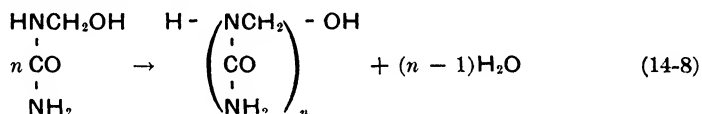
1436. Their hardness, water-whiteness, and color stability even at relatively high (baking) temperatures early suggested the use of urea resins in surface coatings. But ordinary urea resins are not soluble in organic surface-coating solvents even at low levels of resinification, and

furthermore they form brittle films. These objections had to be overcome before success in the surface-coating field was attained.

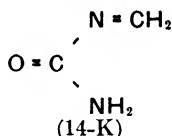
1437. Urea-Aldehyde Reactions. In the presence of electrolytes, especially alkaline catalysts, urea condenses with formaldehyde at temperatures around 30 C to form monomethylol and dimethylol urea.



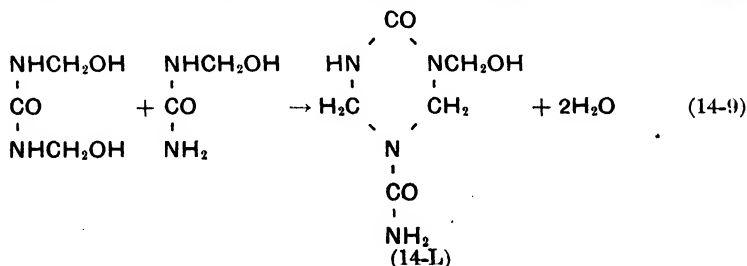
These resinoids may be isolated in pure form. They are colorless and, as might be expected, extensively soluble in water and warm methanol. They are, of course, capable of condensation to high polymers and some of their applications as molding resins, adhesives, and treating agents for wood and textiles have been discussed previously in Secs. 812 *ff.*, 849 *ff.*, 943, and 1142. The polymerization is strongly catalyzed by acids. Direct condensation of molecules of monomethylol urea may result in the following chain formation:



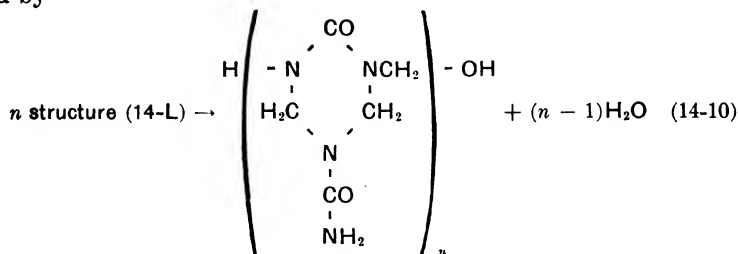
If dimethylol urea is also present, cross-linkage occurs since this compound is capable of polymerizing into two chains. There is considerable evidence that methylene urea [structure (14-K)]



may form from methylol ureas by the loss of water and formaldehyde. Addition polymerization of this compound would lead to the same chains suggested in Eq. (14-8). Other plausible mechanisms have been suggested involving the preliminary formation of cyclic functional compounds followed by the formation of chains containing 6-membered rings,

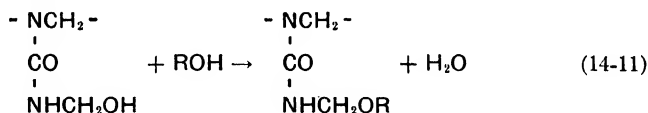


followed by



There is strong likelihood that in the actual process all the above reactions and still others may proceed concurrently or in series. For example, ether linkages may form via the splitting out of water between methylol groups. At any rate, it is an important fact that, in making thermo-setting urea resins, close to 2 moles of formaldehyde is reacted with 1 of urea and that, in their compression molding, a breathing period is provided to permit the escape of steam. Another fact to be borne in mind is that a urea-aldehyde polymer, whatever the reaction mechanisms involved, is left with a considerable amount of polar hydrophilic groups in its structure.

1438. Urea Resins for Surface Coatings. Urea-aldehyde resinoids [Eq. (14-7)] and low-stage urea resins are not soluble in organic surface-coating solvents since they are too strongly hydrophilic. It has been found that, by condensing these compounds with butanol or a higher aliphatic alcohol such as octyl alcohol in the presence of acid, compounds are obtained which are soluble in a wide variety of surface-coating solvents. The reaction may be represented as follows:



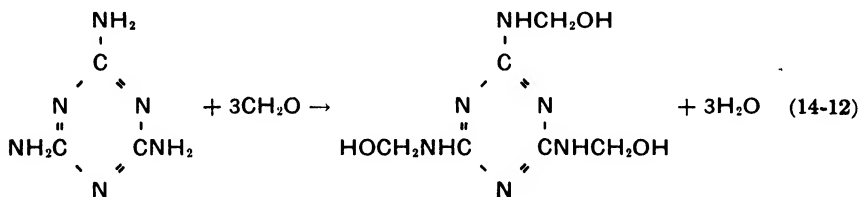
Two things are accomplished. Alkoxy groups are formed, which increase the solubility in weakly polar solvents, and at the same time methylol groups are blocked, reducing the tendency toward cross-linkage into resin molecules too large to be extensively soluble in surface-coating solvents.

The resulting products, known as *alcohol-soluble urea resins*, are too brittle to serve as surface coatings per se but are excellent hardeners for other coating polymers.

1439. Melamine-Aldehyde Resins. Melamine-formaldehyde resins were developed by the manufacturers of urea resins to provide thermo-setting-type compounds that could more successfully compete with the phenolic resins for heavy-duty plastic applications.

Whereas urea is potentially tetrafunctional with regard to condensation, melamine [Eq. (14-12)] is potentially hexafunctional, thus affording more potent cross-linking possibilities. Its reactions with formaldehyde are in many ways analogous to those of urea. The melamine resins differ from the urea resins in that they are harder, more water-resistant, may be baked to a thermoset stage more rapidly and withstand higher temperatures without discoloration, and may be successfully combined with a greater variety of fillers to produce materials of outstanding heat and arc resistance.

Like urea, melamine reacts with formaldehyde in alkaline solutions. Various colorless hydrophilic methylol melamine resinoids may be isolated; as many as six molecules of formaldehyde may be condensed with one of melamine. The formation of trimethylol melamine is shown in Eq. (14-12).



Hexamethylol melamine is the most stable of the resinoids. The complete substitution limits the possibility of polymerization to the formation of ether linkages. Trimethylol melamine is more reactive and polymerizes readily unless kept at low temperatures. The reactions involved in polymerization of the resinoids are probably several in number and similar to those of urea-aldehyde condensation.

Melamine resins may be used to produce molded and laminated plastics of superior properties (Appendix C) as well as hot-setting glues of considerable strength and resistance to hot water. Three per cent melamine resin in emulsion form incorporated in the beater during the preparation of a white absorptive paper pulp results in a paper whose wet strength is nearly as great as its dry strength. There is no accompanying embrittling effect, and the fold resistance may be increased several hundred per cent.

Like the ureas, melamine resins may be used for improving crush resistance and other properties of textiles. In the same manner as methylol ureas, methylol melamines react with alcohols to form compounds extensively soluble in common organic solvents that are suitable for surface-coating formulations [Eq. (14-11)]. The use of methylated methylol melamines for the shrinkproofing of wool was cited in Sec. 1142. Surface-coating applications are discussed in the next section.

UREA-ALKYD AND MELAMINE-ALKYD SURFACE COATINGS

1440. By combining alcohol-soluble urea- or melamine-aldehyde resin with a compatible polyester (alkyd) resin, enamels of outstanding merit are obtained, possessing a happy combination of the best features of both. The polyester acts as plasticizer for the urea or melamine resin; the latter acts as hardener for the polyester. The resulting surface coatings, which are outstanding in hardness, toughness, mar resistance, gloss, richness of color, color stability, adhesion, and outdoor durability, are among the most important in the field. They are widely applied to automobile bodies, refrigerators, stoves, washing machines, signs, etc.

Since the urea and melamine resins polymerize on heating, these enamels must be baked to obtain full cure. Furthermore, as pointed out in Secs. 1404 and 1416, thermal cure of oxidizing-type varnish coatings results in improved film toughness, chemical resistance, durability, and adhesion. Hence, although these enamels may be made in both air-drying and baking types, the baking types develop the best properties. Infrared baking is rapid and particularly advantageous. A typical formulation is shown in Table 14-8.

When maximum color retention and freedom from yellowing are desired, saturated polyester resins are used. Some sacrifice in drying rate has to be made. On the other hand, for rapid drying, maximum toughness, adhesion, and outdoor durability, the relatively unsaturated alkyd resins are better. Compared with the ureas, melamine-resin

TABLE 14-8. WHITE UREA-ALKYD BAKING ENAMEL

Component	Wt %
Titanium dioxide.....	15.0
Zinc oxide.....	5.0
Urea resin (50 % solution).....	10.0
<i>Grind with</i>	
Castor-oil alkyd resin (50 % solution).....	11.0
Butanol.....	3.0
Xylol.....	3.0
<i>Add</i>	
Urea resin (50 % solution).....	19.0
Castor-oil alkyd resin (50 % solution).....	20.5
Butanol.....	3.0
Hydrocarbon.....	10.5
Total.....	100.0

Total solids, 50 per cent. Apply by spray gun. Bake for 1 hr at 250 F.

constituents cure somewhat faster, are more generally compatible with the polyesters, and yield films of somewhat greater hardness, greater outdoor durability, and outstanding gloss and color retention.

Baking times depend on temperature and for many types vary from

about 1 hr at 250 F to 10 to 15 min at 350 F. More recently, catalysts soluble in the enamel solvents have been developed that have made much lower baking temperatures possible and have thus extended the range of application for these finishes considerably.

WATER PAINTS

1441. As the name implies, a water paint is one in which water is the main liquid medium. The most primitive example is whitewash, an aqueous dispersion of slaked lime. The term *calcimine* usually implies whitening as the principal pigment, animal glue or dextrin as the binder, and water as the vehicle.

Experimental investigation pointed toward the development of good water paints are continually in progress. They rest on sound grounds since such paints possess several inherently attractive advantages, among which are elimination of the odor, fire hazard, toxicity, and cost of organic solvents, as well as applicability to damp or wet surfaces.

1442. Casein and Oleocasein Paints. Calcimine is not washable since the binder is water-soluble. It was early discovered that better water resistance could be obtained by substituting a mixture of casein and lime for part or all of the animal glue. Casein, a protein, disperses readily in dilute aqueous solutions of alkalis or alkaline salts. Excess alkaline-earth hydroxides cause eventual precipitation and hardening. Many casein paints (of the dry-powder type) thus depend upon the presence of excess lime to produce a hard, relatively insoluble surface-coating film. Formaldehyde or hexamethylenetetramine may likewise be used for this purpose. In this instance, hardening depends on the formation of cross-links via the coupling of amino groups of the casein [Eq. (11-6), page 494].

Casein paints have been marketed in two main forms, dry powder and paste. The latter are usually of a consistency that permits dilution with about half a volume of water prior to use. The formulation for a typical dry-powder paint is shown in Table 14-9.

TABLE 14-9. CASEIN DRY-POWDER PAINT

Ingredient	Lb	Gal
Lithopone (28 % ZnS).....	53.6	1.496
Magnesium silicate.....	18.4	0.774
China clay.....	7.0	0.321
Lime, Ca(OH) ₂	11.0	0.647
Casein.....	10.0	0.955
Total.....	100.0	4.193

Add 10 gal of water immediately prior to use.

It is interesting to compare the weight and volume compositions of this typical casein paint (Table 14-10) with those of oleoresinous paints and enamels (Table 14-6). Counting the lime as both part of the pigment and the ultimate binder, the pigment-binder volume ratio of this paint is about 2, which places it in the class of flat finishes (Table 14-7). True casein paints are limited to flat and mat finishes.

TABLE 14-10. COMPOSITION OF A TYPICAL CASEIN PAINT

Item	Wt %	Vol %
Binder (casein).....	6	7
Pigments.....	49	23
Water (volatile solvent).....	45	70

The dry-powder and paste types each exhibit advantages and disadvantages. The dry-powder type bears excess lime or other hardening agent without setting during storage or unduly corroding the container. The film laid down from it will harden without special treatment. However, the range of colors is limited to those which are not attacked by excess alkali. By contrast, the paste type cannot carry excess alkali or hardening agent. Furthermore, an effective preservative must be added to prevent bacterial attack of the casein. Finally, to obtain a hard, relatively insoluble coating, washing with formaldehyde after application is required. This is a nuisance, involving extra labor and expense. To compensate for these shortcomings there is the advantage of a wide range of vivid colors such as cannot be attained in the dry-powder type.

The following advantages over flat oil paints are claimed for water paints:

1. Elimination of odor, fire hazard, toxicity and cost of organic solvents
2. Applicability to damp surfaces
3. Greater ease and lower cost of application for the following reasons:
 - (a) Porous surfaces need not be sealed prior to application.
 - (b) Owing to less "drag," these paints may be applied faster with larger brushes.
 - (c) Hiding is attained with fewer coats.
4. Greater drying speed (second coats are applicable in 1 to 3 hr)
5. Production of a uniform flat finish (there is no tendency for streaks of greater gloss to appear)
6. High hiding power
7. Colors of outstanding lightness (Sec. 1428)
8. Little or no tendency toward after-yellowing

Against these advantages, casein paints have been criticized for lower washability and durability than flat oil paints. They have been applied

mainly as interior finishes, and even here an aging period of 30 days or more is usually recommended prior to any washing of the surface.

The desire to minimize the above shortcomings has led to a compromise product, the *oleocasein paint*, in which the binder consists of casein plus oleoresinous constituents. The latter are incorporated by emulsification, suitable emulsifying agents being soaps or like materials. By this procedure, washability and durability may be considerably improved, but the cost of manufacture is increased, and hiding power, color brilliance, and freedom from after-yellowing are partly sacrificed.

Casein water paints are of inherently low consistency and yield value, and in many of them there is a tendency toward settling and severe caking of the pigments (Sec. 1427). The emulsification of oleocasein paints therefore serves another useful purpose in that it imparts thixotropic body to the product, which tends to minimize settling and caking. Water-soluble gel-forming materials such as soaps, agar, and gum tragacanth are employed in straight casein paints for the same purpose.

1443. Alkyd-emulsion Paints. Of more recent development are the *resin-emulsion paints*, which possess durability and washability approaching those of flat oil paints, the most serious criticism directed at water paints being thus removed. They are usually made by emulsifying an alkyd resin (specially made for this purpose) in an aqueous medium, generally a protein solution. Casein is often the protein employed. When the emulsion is applied to a surface, water evaporates, the emulsion breaks, and a continuous alkyd-resin surface coating forms. The ultimate drying is almost invariably of the oxidative type. The final film contains all the solids originally dispersed, including the emulsifying agents. Since most of these agents are hydrophilic, the durability and water resistance of the final film are influenced by their character and concentration.

The entire success of these paints rests on the production of a highly stable emulsion. This involves special manufacturing procedures and the use of drying-oil-modified polyester resins, in many instances specially developed for the purpose. In a good emulsion the dispersed droplets are all below $1\ \mu$ in diameter, with at least 25 per cent below $0.5\ \mu$. The droplet size influences not only emulsion stability and settling but also the flow properties and brushability. Formulations are shown in Table 14-11, and the weight and volume compositions of the same paints ready for application are presented in Table 14-12 (compare with Tables 14-6 and 14-10).

The alkyd-emulsion paints combine many of the advantages common to water paints with superior durability and washability. There is no odor or fire hazard during painting, they are easy to apply, they may be

put on porous and wet surfaces, and, in favorable weather, two coats may be applied the same day. However, freedom from yellowing is not so complete as in casein paints, and there is always danger of emulsion breakage during storage or on the brush. When the latter occurs, resin accumulates on the bristles and the brush grows progressively stiffer and must eventually be cleaned with organic solvent.

TABLE 14-11. TYPICAL ALKYD-EMULSION PAINTS*

Component	Lb	Wt %
Exterior White. Paste†		
Titanium dioxide (water dispersible).....	100	15.4
Barium titanium pigment (extra strength).....	100	15.4
Flake mica.....	25	3.8
Silica.....	25	3.8
Alkyd emulsion (50 % solids).....	400	61.6
Total.....	650	100.0
Interior White. Paste‡		
Titanium dioxide (water dispersible).....	200	16.0
Barium titanium pigment.....	200	16.0
Colloidal silica.....	150	12.0
Flake mica.....	50	4.0
Alkyd emulsion (50 % solids).....	200	16.0
Water.....	450	36.0
Total.....	1,250	100.0

* MATTIELLO, J. J., "Protective and Decorative Coatings," Vol. 3, John Wiley & Sons, Inc., New York, 1943. Reprinted by permission.

† For application, reduce each gallon of paste with 1 to 1½ gal of water for a first coat and 3 qt for a second coat.

‡ Reduce each gallon of paste with 1 qt of water.

TABLE 14-12. COMPOSITIONS OF ALKYD-EMULSION PAINTS
(Paints of Table 14-11 ready for application)

	Exterior paint		Interior paint	
	Wt %	Vol %	Wt %	Vol %
Water (volatile solvent).....	60	71	52	73
Binder (resin, protein, etc.).....	18	22	7	10
Pigments.....	22	7	41	17
Total.....	100	100	100	100
Pigment-binder ratio.....	...	0.32	...	1.7

1444. Urea-Formaldehyde Water Paints. Because urea resins at a low stage of polymerization can be made water-soluble and cold-setting,

they afford an attractive possibility as binders for water paints. Since the resins are soluble in water, they need not be emulsified. They may be caused to polymerize to an insoluble film by incorporating water-soluble catalysts. The resins are colorless and free from after-yellowing. It has been claimed at the current writing that water paints of excellent washability and phenomenally rapid drying qualities may be produced. However, owing to the inherent brittleness of urea resins, the durability of the paints may prove open to question.

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MATTIELLO, J. J., *Proc. Am. Soc. Testing Materials*, **46**, 493 (1946).

See also Appendix A.

PARTICULAR TOPICS

See references accompanying tables and figures of this chapter.

Solvents

- MELLAN, I., "Industrial Solvents," Reinhold Publishing Corporation, New York.

CHAPTER 15

ADHESIVES

1500. Generally speaking, an *adhesive* is a substance applied as a thin intermediate layer between two bodies to hold them together by surface attachment. Adhesive is the general term covering cements, glues, mucilages, and pastes. It is usually not applied to metal solders, although the latter are adhesives in every sense. The bodies held together are called the *adherends*. *Substrate* may be used for adherend, although the former is a somewhat broader term applicable to any material on which a coating or film is spread, regardless of function. The term *bonding*, although not wholly satisfactory, will be used to denote the process of joining surfaces by adhesive action. Regardless of the nature of the adhesive, the adhesive layer together with the adhesive-adherend interfaces is usually called the *glue line*.

Practically all commercial adhesives are polymeric materials, particularly because of favorable rheological characteristics. For proper spreading, adhesives are almost always applied in liquid form or at least are liquefied at some stage in the bonding process, so that, to achieve strength and substantial permanence, setting must take place. The setting of an adhesive may involve a simple evaporation of solvent, absorption of solvent by a porous adherend, sol-gel or liquid-solid transitions, a polymerization process, or combinations of these. During setting, the joint strength increases, in many cases ultimately surpassing that of the adherends themselves.

The development of adhesives has been largely empirical. Only in recent years has a partly satisfactory understanding of the physical and chemical factors involved in adhesion been achieved. As with surface coatings, one complication is that, in an adhesive joint, the adhesive is present as a thin film, often oriented, whose physical and chemical behaviors may be notably different from those predicted from studies of the same material *en masse*. Some aspects of this subject have already been discussed in Chap. 14, since surface coatings are merely thin films that must adhere to one surface, while adhesives are thin films that must firmly join two.

THE CHARACTER OF AN ADHESIVE JOINT

1501. The two requirements for adhesive joint formation are adhesion at the interfaces between adhesive and adherends and cohesion or

strength within the adhesive layer itself. This is aptly illustrated by water and wood. Owing to the similarity in polarity and chemical properties of water and cellulose, the adhesion between them is excellent, as shown by the ease of wetting, etc. Nevertheless, if liquid water is used as an adhesive for wood blocks, the joint has insignificant strength. However, when the water is converted to ice by lowering the temperature, the joint becomes so strong that, on testing, failure occurs in the wood and not in the adhesive layer of ice.

When a bonded assembly is subjected to stress, it may fail (1) at either of the two adhesive-adherend interfaces against adhesive forces or (2) within either adherend or the adhesive layer against cohesive forces. There are thus essentially five possible regions of failure. Actual rupture will occur in the weakest "link" of the assembly.

When an adhesive is discovered that gives a bonded joint sufficiently strong and durable to replace mechanical assembly by such devices as screws, rivets, bolts, dovetailing, or undercutting, this often represents a major advance in engineering practice. Production costs are reduced, and distributed loading replaces point loading. In the case of metals, an organic adhesive may eliminate bimetallic contact and attendant corrosion.

ADHESION

1502. Adhesion Mechanisms and Factors. Two mechanisms are commonly postulated for adhesion, *mechanical adhesion*, which is a mechanical gripping or interlocking, and *specific adhesion*, attributable to intermolecular forces (Secs. 216 and 1414 ff.). The improvement in adhesion often encountered when adherend surfaces are roughened is presumed evidence for the first, while the fact that it is possible to get excellent adhesion to dense, mirror-smooth surfaces is best explained by the second.

The preponderance of evidence indicates that mechanical adhesion is of no importance except for porous adherends, and even here it probably is not the major factor. Joint strength attributed to it in the past is, in fact, often traceable to other effects. For example, roughening of an adherend appears to improve bonding by increasing the total available surface area or by exposing fresh, clean surfaces with strong unbalanced valence forces, rather than by affording any purely mechanical interlock. A case in point is the experimental fact that sanding wood surfaces with very fine sandpaper immediately before gluing results in a stronger bond than that obtained either with glazed surfaces produced by planing or with roughly sanded ones.

In some cases, primary-valence bonding is involved; in others, secondary-valence bridging is responsible for specific adhesion. The importance

of surface behavior reaches a peak when an adhesive is required to bond two adherends of different character and hold them together with considerable force. In broadest terms, adhesion depends upon (1) the surface forces inherently available at the joint, as determined by the physical and chemical nature of adhesive and adherend, (2) the condition of the surfaces at the time of bonding, as controlled by the method of their preparation or formation, and (3) the conditions prevailing when the joint is formed—temperature, pressure, humidity, etc.

1503. Surface Forces. The origin of surface forces and some of their consequences have already been discussed (Sec. 216). Ordinarily, the surface is at a higher energy level than the interior of the mass, owing to unbalanced, unsaturated valence forces. This produces a variety of effects. To recall just one, solutes that reduce surface tension will concentrate in the surface.

Broadly speaking, an adhesive should be selected in accordance with the chemical nature of the adherend surface, *e.g.*, a nonpolar adhesive for hydrocarbon rubbers, a polar adhesive for woods. Obviously, the adhesive should wet the surface, spread well, and, in the case of porous adherends, penetrate to the proper depth. If the chemical nature of the adhesive is correct, wetting will take place provided that the surfaces have been adequately cleaned or conditioned. The above considerations are fundamental but of little help in the final selection of an adhesive for an actual practical application, for two adhesives fulfilling the above requirements may produce joints of enormously different quality owing to basic differences in the chemical and mechanical properties of the adhesive layer itself.

High specific adhesion of the set adhesive to the adherend is obviously indispensable for a strong joint. In addition, high specific adhesion during the liquid stage is desirable to prevent squeezing out of the adhesive on application of pressure (Sec. 1507).

1504. Conditioning of Surfaces. In plating, coating, and bonding, the condition of the surface is a vital factor. Flakes of split mica adhere tenaciously if the split surfaces are immediately rejoined; but if they are exposed to the atmosphere for even a few minutes, this property is lost. The superior glue bond obtained on wood freshly sanded with fine paper has already been cited. Such results indicate that a clean, freshly exposed surface contains strong attractive centers which, owing to their very activity, may soon be saturated via adsorption or reaction with any material to which they happen to be exposed, *e.g.*, the ambient air. Therefore, good practice often demands that adherend surfaces be freshly prepared. Besides its fixed components, the atmosphere normally contains variable amounts of moisture, organic matter, carbon

dioxide, and sulfurous gases. Tarnishing, rusting, oxidation, hydrolysis, "filming," "aging," and "grease pickup" are specific and loose terms for describing what happens to surfaces exposed to air.

In this field the term *contaminant* should be reserved for materials which actually interfere with proper adhesion, and we shall define a *clean surface* as one the physical and chemical constitution of which is proper to the success of the process at hand.

The surfaces of many molded plastic products are inert and difficult to join. This is often traceable to adsorbed mold lubricant. Another possible cause is that the reactive groups of the polymer become inwardly directed if polymerization takes place in the mold owing to the absence of attractive groups on the (steel) mold walls. Phenoplasts are unusually difficult to join. Removal of the top layer exposes more reactive surfaces that give somewhat better adhesion. Removal of the surface layer of molded plastics containing cellulosic filler exposes a fuzz of fibrous cellulose. The attendant improvement in bonding is attributable to specific adhesion afforded by the hydroxyl groups and perhaps partly to mechanical adhesion afforded by the anchored fuzz.

Some pairs of adherends differ so widely in chemical and structural properties that suitable adhesives have not been found. It then becomes necessary deliberately to alter the surface composition of one of the adherends. This may be done by chemical reaction or the application of a coating. A case in point is steel and rubber. Engineering application demands the joining of these two materials by strong bonds as in the case of the bead of tire tread. In this instance, the steel is plated with a thin coating of brass. The rubber is then vulcanized in contact with the brass-coated steel. The resulting adhesion is excellent owing to the formation of primary-valence copper sulfide bonds between the copper of the brass and sulfur of the rubber. This type of procedure is analogous in many ways to phosphating and chromate priming in the surface-coating field (Sec. 1416).

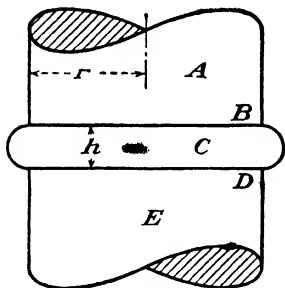
The very important question as to whether an adherend should be prepared with a rough or smooth surface involves complex factors indicated in Sec. 1507.

TACKINESS

1505. Tackiness means different things in different industrial fields. When the term is applied to an adhesive, it means the resistance which must be overcome to separate two solid adherends between which there is an adhesive still in its liquid state.

Assume an assembly as in Fig. 15-1 composed of two circular rods *A* and *E*, between which there is a layer of liquid adhesive *C*, which bulges out at the periphery. This bulge may be thought of as a reservoir of

excess liquid. When a tensile pull is applied to the rods normal to the interfaces, liquid adhesive is sucked in from the bulge. The liquid layer increases uniformly in thickness till the bulge disappears. Thereafter, further separation of the rods causes the liquid to neck down, thread out, and finally part. The stress applied to the rods is the same as that required to overcome the liquid's internal resistance to flow and cause it to move in from the bulge. As long as liquid is still present in the bulge, the following equation applies:



*A and E = Solid adherends
B and D = Adherend-adhesive interface
C = Layer of liquid adhesive
h = Thickness of adhesive layer
r = Radius of specimen*

FIG. 15-1. An adhesive joint. [J. J. Bikermann, *J. Colloid Sci.*, **2**, 163 (1947).]

$$st = \frac{3\eta r^2}{4} \left(\frac{1}{h_1^2} - \frac{1}{h_2^2} \right) \quad (15-1)$$

where s is the applied tensile stress, t the duration of its action, *i.e.*, the action time, η the viscosity of the adhesive, r the radius of the specimen, h_1 the initial thickness of the adhesive layer, and h_2 its thickness after time t .

Equation (15-1) is called the *tackiness equation*. Its derivation assumes that the adhesive is a Newtonian liquid. The conclusions below follow from this relation:

1. There is an unusual feature in that the unit stress depends upon the area; *i.e.*, doubling the area quadruples the tensile stress or multiplies the force required to part the assembly eightfold. This is because the entire bulk of the liquid sample is involved and moves when stress is applied.
2. There is no one value for the force opposing the breaking of the joint. The resistance to separation depends on the rate of separation.
3. The entire separation process occurs within the liquid layer. The forces acting between the adhesive and the adherends A and E are not involved at all. The phenomenon is purely rheological.
4. The product st is larger the smaller the original thickness of the adhesive layer, h_1 . Under the assumptions the product st will be inversely proportional to the square of the thickness of this layer.
5. The product st is proportional to the viscosity of the adhesive layer. Hence, for high tackiness, channels of air in this layer must be avoided since gases have negligible viscosity.
6. It is apparent that the quantity s is inversely proportional to t . When t is very small, *i.e.*, when the joint is broken with a jerk, s may become greater than the ultimate strength of one of the adherends, causing rupture to occur within the solid. This behavior is common when

the adherends are of low strength. Thus, slow stripping will successfully remove a freshly applied postage stamp, while rapid stripping will tear either the stamp or the paper to which it has been applied.

Numerical examples are revealing. Let A and E be 1 sq in. in cross section, h_1 0.001 in., h_2 0.01 in. or larger, η 10 poises, which is approximately the viscosity of most freshly applied adhesives. st is then 100 psi-sec. If t is 1 sec, then s is 100 psi. As the adhesive sets, its viscosity increases. When the viscosity becomes very high, Eq. (15-1) loses its quantitative validity because the adhesive is no longer Newtonian. Nevertheless, it may be used qualitatively. When the viscosity reaches 10^4 poises, which is characteristic of low polymers (Table 7-8), the computed tensile stress is 1,000,000 psi. Even if the solids are separated over a period of 10 sec, the stress required is still 100,000 psi. Of course, no such stresses would be reached in fact since the assembly would fail in tension long before this in layers A , C , or E or at the interfaces B and D .

Tackiness has far-reaching practical importance. A so-called "pressure-sensitive" adhesive is one that can be made to adhere satisfactorily to a surface by finger pressure. Cellophane ("Scotch") tape, surgical tape, masking tape, and electrical tape are familiar examples of important products employing adhesives of this kind. The uses to which these materials are put do not require great ultimate bond strength, nor are the products normally subjected to prolonged stress after application. Indeed, their function is commonly to supply a temporary bonding action, and it is a desirable feature if these adhesives may be removed, after discharge of their temporary function, without damage to the substrate. For these materials, adequate bonding may be achieved through tackiness of a substantially "liquid" adhesive so that Eq. (15-1) is pertinent. It is not essential for these adhesives ever to set.

Tackiness is often important to high-strength adhesives also. A sufficient amount of original tackiness makes possible the preassembling and preliminary handling of assemblies before the adhesive sets to form the final bond. It also minimizes the danger of starved joints (Sec. 1507).

COHESION

1506. The Setting of Adhesives. It has previously been pointed out that a bonded assembly may fail against either adhesive or cohesive forces. In all of what may be called structural assemblies the adhesive joint is subjected to continuous or intermittent external stress in service. Consequently, the adhesive must set, both to attain adequate strength and to reduce creep and relaxation.

An adhesive may set by cooling, loss of solvent, polymerization, etc. At some point it may be said to have solidified. In this field, differentia-

tion between "liquid" and "solid" is made on the basis of the type of failure that occurs in the adhesive layer of the assembly.

1. The adhesive is liquid and there is *liquid-type failure* when Eq. (15-1) applies qualitatively if not quantitatively. Rupture occurs via the mechanism of flow; and as the tackiness equation shows, it depends on the consistency of the adhesive and on the shape and dimensions of its bulk. Tensile strength increases roughly as the square of the cross section.

2. The adhesive is solid and there is *solid-type failure* when the consistency is such that substantial inward flow of the adhesive from the periphery of the joint (Fig. 15-1) does not take place when tension is applied to the assembly. Rather, failure occurs via the initiation of a crack at a weak spot and its propagation within the adhesive layer. In other words, flaw factors assume prominence (Secs. 900 ff.). To a first approximation the tensile strength is now independent of the cross section. Indeed, it may decrease with increase in area because of the flaw-probability factor (Sec. 906). As in liquid-type failure, resistance to tension decreases with increase in thickness of the adhesive layer but for different reasons (see Sec. 1507).

In liquid-type failure the sole intrinsic property of the adhesive contributing to the parting strength of the joint is its viscosity [Eq. (15-1)]. Hence, two adhesives of equal viscosity yield the same parting strength regardless of composition, constitution, etc., provided only that they both properly wet the adherend surfaces. By contrast, in solid-type failure many properties of the adhesive contribute to the joint strength, among them tensile strength, shear strength, notch sensitivity, freedom from flaws, moisture resistance, aging qualities, and coefficient of expansion.

1507. Thickness of Adhesive Layer. The thickness of the adhesive layer is an important determinant of the ultimate parting strength in all adhesive layers. If too little adhesive is applied (especially likely when adherends are porous), a weak joint results from lack of film continuity. The joint is said to be *starved*. On the other hand, thicknesses greater than necessary to give a continuous film result in lower parting strength due to hydraulic factors in liquid adhesives and flaw factors in solid adhesives (Table 15-1 and Sec. 905).

It is thus usually desirable to have as thin a layer of adhesive as compatible with film continuity. In most practice, adhesive is applied liberally and the excess, along with air bubbles, squeezed out under pressure. Too high a pressure or too low a consistency in the adhesive results in starved joints. Finely divided solid fillers, often added merely to decrease cost, increase the consistency of the adhesive and may thus

influence film thickness, but their effect on the strength of the adhesive in its final set form is of much greater intrinsic significance.

TABLE 15-1. JOINTS STRENGTH VS. THICKNESS OF ADHESIVE LAYER

Joint	Thin, 57 μ psi	Thick, 540 μ psi
Al:shellac:Al.....	2,060	1,070
Ni:shellac:Al.....	2,700	1,560
Brass:paraffin:steel.....	350	210
Wood:glue:wood.....	1,200	600

Data from several sources.

For obvious reasons, uniform over-all thickness is desirable in the adhesive layer. This is most readily achieved with adhesive in the form of film (Sec. 1510).

Some adhesives are relatively insensitive to flaws. Their notch sensitivity is low so that they lose relatively little strength with increased thickness. These are called *gap-filling adhesives*. The gap-filling property is often of great commercial value because it increases allowable tolerances in the trueness of adherend surfaces and misalignments of surface likely to be encountered in manipulation. A high proportion of volatiles in the adhesive reduces gap-filling properties owing to the voids formed during evaporation and setting. Rubbery and plastic adhesives are more likely to be gap-filling than brittle ones.

A smooth adherend surface may be more desirable than a rough one because the depressions require a thick layer of adhesive and may also trap air. In the opposite direction, roughening provides greater area of contact between adherend and adhesive. Consequently, the relative merits of smooth and rough surfaces depend on the mechanism of failure. If the failure is *within* the adhesive layer, the smooth surface is indicated because it decreases the thickness of the adhesive. On the other hand, if failure occurs against forces of adhesion acting at an adherend-adhesive interface, a rough surface is better since it provides greater interfacial area.

SERVICE LIFE OF ADHESIVE JOINTS

As with surface coatings, so also with adhesives. Once an adhesive joint has been bonded, various factors begin to operate toward its breakdown.

1508. Coefficients of Expansion. The range of the coefficients of thermal expansion of organic high polymers lies above that of the metals, which in turn is higher than that of ceramics and glass (Table 10-4). For wood, a highly anisotropic material, the coefficient is about ten times

as great across the grain as it is along it. When adherends and adhesive have unlike coefficients, temperature fluctuations cause unequal expansions and contractions. The stresses set up may cause rupture at interfaces or within the adhesive layer, and this is one of the most powerful causes for the deterioration of joint strength. There is a trite and oversimplified maxim to the effect that "the best adhesive for a material is the material itself." Its main element of truth lies in the fact that in such a joint the unequal-expansion factor would be eliminated.

When the two adherends have markedly different coefficients of expansion, it is absolutely essential for the adhesive to possess sufficient rubberiness or plasticity to take up the strains accompanying thermal fluctuation. Good gap-filling properties are also desirable. It is furthermore helpful in such case to roughen the adherend surfaces markedly so as to have much of the adherend surfaces at an angle to the joint. This minimizes the effect of temperature change, for reasons of geometry.

When the two adherends have essentially the same coefficient of expansion which is different from that of the adhesive, it is particularly desirable to have a thin layer of adhesive, in which case the latter will have so little substance parallel to the joint that it will expand or contract with the adherends, rather than by its own coefficient of expansion.

Humidity changes may act similarly to temperature fluctuations if different degrees of swelling due to moisture absorption occur in adherend and adhesive layers.

1509. Aging. Deterioration in an adhesive joint may be caused by one or more of a variety of long-time effects grouped under the term aging.

Some adhesives literally dry out. Eventual loss of too much plasticizer or solvent may cause excessive shrinkage, brittleness, or both. Almost everyone has observed instances of such adhesive failures at first hand.

Crystallization starting at points within an originally amorphous layer is accompanied by densification at those points. Flaws and cracks may eventually result, much as in surface-coating films (Sec. 1423).

Chemical breakdown may eventually occur within the joint because of slow reaction with moisture, oxygen, or other atmospheric constituents. The greatest drawback of most adhesives of biological origin such as starches, dextrans, soybean, animal glue, and fish glue is that they are attacked chemically and by microorganisms, particularly in moist environments.

CHARACTER OF THE ADHESIVE

The properties of an adhesive must be considered under two main categories, those which are important before and during application, and those which are of consequence after application.

1510. Keeping Qualities. An adhesive should contain active groups that will not only combine with the bond-forming centers in the adherend surfaces but also displace contaminants likely to be present at those surfaces. However, active groups in the adhesive must be kept within limits for the following reasons:

1. They usually increase cohesion within the ultimate adhesive layer, reducing its plasticity and increasing its brittleness. If carried too far, this may result in a weak joint.

2. Too many active groups may promote internal reaction, or aging, thereby decreasing the storage, or "pot life," of the adhesive.

3. Increasing the active groups may even decrease adhesion to the substrate. For example, sodium silicate solutions are widely used for gluing paper cartons. Since the adhesion is primarily between the hydroxyl groups of the adhesive and those of the cellulose, colloidal silica might seem to be an even better adhesive. However, it begins to "age" immediately on formation, the free hydroxyls interacting by condensation and thus soon decreasing the total number available. Although this reaction also occurs in freshly prepared sodium silicate solutions, the aged solutions are left with Si—O—Na groups, which hydrolyze readily on contact with cellulose, producing fresh hydroxyl groups which form excellent bonds.

Adhesives are marketed in several physical forms.

Liquid. This form is convenient in that it requires no preparation. It is employed widely in industry as well as in retail packages for the household. However, the solution form can be used only for adhesives that do not age rapidly.

Powder. Rapid-aging adhesives keep better in dry-powder form, to which solvent or dispersing agent is added shortly prior to application.

Split-batch. Active adhesives whose setting involves chemical reaction are often made up in two components, particularly if they set at room or moderate temperatures. Frequently one of the components is a catalyst. The components are kept in separate containers and are mixed immediately before use.

Film. Adhesives may also be put up in film form, which is made by saturating thin paper with a solution of low-stage resin, after which the solvent is driven off, the resin advancing to a nontacky stage. An example is Tego film, which contains a hot-pressing phenolic adhesive. When laminates are bonded by laying up plies properly interleaved with such film, starved joints and thick spots, such as might occur by manual application of adhesive in liquid form, are avoided (Sec. 1507). Other advantages are that film can be handled cleanly and rapidly. These advantages often justify the added cost.

1511. Molecular-weight Factors. There is ample evidence that, with linear-thermoplastic adhesives, best bonding properties and highest joint strengths are obtained when the average D.P. has a particular value which is neither very high nor very low (Table 15-2). Thus, the strongest

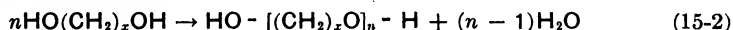
TABLE 15-2. MOLECULAR-WEIGHT RANGES FOR GOOD ADHESIVE PROPERTIES
D.P. Ranges for Good

Polymer	Adhesion
Polyvinyl acetate.....	60-200
Polyvinyl chloride-acetate.....	100-150
Polyethyl acrylate.....	80-150
Polyisobutylene.....	50-150
Polyamides.....	50-100
Cellulose nitrate.....	150-300
Chlorinated rubber.....	125 centipoise grade

DELMONTE, J., "The Technology of Adhesives," Reinhold Publishing Corporation, New York, 1947.

starch adhesives are prepared by an acid pretreatment (hydrolytic degradation) followed by treatment with alkali (oxidative degradation), which not only degrades but also introduces oxygenated functional groups along, as well as at the ends of, the chains [Eqs. (4-44) and (4-45), pages 142, 143]. Vinyl polymers show best adhesive properties in an intermediate-to-low range (Table 3-3, page 87). Animal glues are partly hydrolyzed proteins; the grades which are intermediate in gel strength and viscosity yield the strongest adhesive joints. The best polyisobutylene adhesives are not the toughest ones of highest molecular weight but the intermediate, more plastic fractions. Better results are often obtained from samples with a broad molecular-weight distribution than from closely fractionated cuts of the same average D.P. These facts are readily analyzed from theory.

For purposes of illustration, let us assume that a linear polyether formed via reaction (15-2) is to be used as an adhesive between polar (hydroxylated) adherends.



At the one extreme, represented by no polymerization whatever, is the monomeric material. This material has the smallest molecules with the greatest mass concentration of polar groups. Viscosity is at a minimum. Solubility, specific adhesion, surface tension, and rate of penetration into porous adherends are at a maximum. (The rate of penetration of a liquid into a capillary varies directly as the surface tension and inversely as the viscosity.) Since the material is liquid, its inherent mechanical strength is negligible. We may regard material at a D.P. value up on the plateau of the strength-molecular-weight curve (Fig. 9-3) as a second extreme. This material is solid. The molecules are very large and in this illustration are devoid of strongly polar structures other than the end groups,

which represent a minute mass concentration. An adhesive layer of this material might have adequate mechanical strength; but specific adhesion to the adherends would be low, and solubility, wetting, and penetration into porous adherends would be at a minimum. Thus, neither of the extremes serves to produce a satisfactory adhesive, but the intermediate range represented by average D.P. values from about 50 to 200 affords a desirable combination of properties.

Still using the above system for purposes of discussion, a broad molecular-weight distribution may be better than a narrow one for the following reasons: A large number yet small weight fraction of very small molecules will be present to promote wetting and specific adhesion. As the adhesive layer sets, the very large molecules will precipitate or gel first. They will contribute greatly to the eventual cohesive strength of the adhesive layer. The more mobile small molecules will form a solution of relatively low viscosity that will not only wet the interfaces but also permit ready displacement of adsorbed air and penetrate rapidly into the adherend. One may thus envision molecules of different sizes discharging functions with peculiar effectiveness at just the desired locations. No such specializations of function could occur if the molecules were all of one size.

Polymeric adhesives may be divided into permanently linear thermoplasts and space-polymerizing thermosets. The latter possess the inherent property that they may be introduced into the joint as small molecules with all the advantages of low viscosity, high wetting power, ready penetration, etc., and then polymerized *in situ* to form cross-linked molecular networks of much higher mechanical strengths than the linear-polymeric types.

1512. Volatiles and Their Release. When an adhesive contains volatile solvent or dispersing agent, and the majority of them do, the release of this volatile material is of great consequence. Let us consider first a room-temperature operation. For optimum results a rather critical control must be maintained over the amount of volatile present when the assembly is first closed. If too little is present, the fusion of two spread surfaces or the wetting and transfer from a spread to an unspread surface will be incomplete. If too much is present, excess volatile material may be trapped in the closed assembly and weaken the final bond by overplasticization and/or void formation. The operating schedule must be such that it includes the optimum time interval between spreading and closure. This is important in all cases but less critical for space polymerizing than for permanently linear-polymeric adhesives. Obviously, underdrying is less critical for porous adherends like wood than for impenetrable adherends.

If both adherends are impenetrable like glass or metal, the only way to attain maximum joint strength is to expel all volatiles after spreading and then resort to the application of heat to get proper fusion and adhesion upon closure of the assembly.

Solvents for adhesives may be divided into water on the one hand and organic solvents on the other. Water is inexpensive, nonflammable, and nontoxic. These advantages are imparted to water-soluble adhesives. However, water-soluble glue lines are always subject to breakdown on exposure to a moist environment. They may successively swell and shrink with changes in humidity, and those of animal and vegetable origin may undergo microorganism or chemical attack when moist. This is an inherent weakness of dextrans, starches, gums, casein, and hide and blood glues, and it precludes them from certain important fields of application. Many organic solvents evaporate more rapidly than water. Organosoluble adhesives are less likely to be sensitive to atmospheric changes.

Volatiles in the adhesive must not act adversely on the adherend. If sheets of writing paper are joined with a water-borne adhesive, the paper wrinkles badly at the joint. Moreover, it loses its finish because of the swelling and displacement of the cellulose fibers. When it is subsequently written on with ink, the latter spreads and blurs. These detriments are avoided when an organosoluble rubber adhesive is used. Volatiles are particularly likely to damage thermoplastic adherends.

Emulsification may be invoked to retain the advantages of a water vehicle with an organic adhesive. Many latices are used. Emulsification also makes applicable otherwise chemically incompatible combinations such as rubber and casein. After spreading, the emulsion breaks in a short time, forming a sticky surface film, permitting rapid assembly. The storage life is inclined to be short owing to instability of the emulsion.

1513. Setting Characteristics. Although one does not ordinarily consider them as such, all binders used in molded binder-filler products are, in the final analysis, adhesives of an "all-through" type. Consequently, the same factors are of fundamental importance in molding, laminating, and bonding, *viz.*, temperature, pressure, and time. And whereas surface conditioning is often a final step for a molded product, it is a preliminary step in bonding.

At any rate, as in molding, the cost of bonding decreases as cycle time and surface preparation are minimized and working pressures and temperatures are reduced toward room conditions. In most, though not all, cases, the cost of the glue is of secondary consequence.

Adhesives may be

1. Cold-setting,¹ below 68 F

¹ "Cold-setting" used to be synonymous with "room-temperature-setting."

2. Room-temperature-setting, 68 to 86 F
3. Warm-setting, 86 to 211 F
4. Hot-setting, at or above 212 F

They may require

1. Contact pressure, 1 psi or less
2. Low pressure, 1 to 250 psi
3. High pressure, greater than 250 psi

Within the above temperature and pressure framework, adhesives may be classified as in Table 15-3.

TABLE 15-3. CLASSIFICATION OF ADHESIVES BY SETTING CHARACTERISTICS

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- A. Soluble or Fusible Adhesives (linear-polymeric)
1. Solvent-evaporation types
 - a. Solutions. Dispersed in true solvent. Glue line forms upon simple evaporation of solvent
 - b. Emulsions. Adhesive dispersed in nonsolvent liquid, *e.g.*, rubber latices. Makes applicable otherwise chemically incompatible combinations
 2. Thermal-fusion types

Hot melt. Little or no solvent present. Solid at room temperature, liquefiable at temperatures below decomposition point, *e.g.*, hide glue.
 3. Pressure-sensitive types. Semisolid materials that form adequate (low-strength) bonds under the influence of pressure alone
- B. Mutating (space-polymerizing) adhesives
1. Room-temperature-setting. Often require strong catalysts. Common disadvantages are relatively short pot life and open assembly time
 2. Warm-setting. Often contain moderate amounts of catalyst. Pot life usually adequate
 3. Hot-setting. Usually require little or no catalyst. Ordinarily quite stable; long storage life, pot life, and open assembly time
-

The steps involved in bonding are the following. Depending on the type of adhesive and nature of the assembly, some may not be necessary.

1. Preparation of adherend surfaces. Involves cleanliness, degree of roughness and degree of truing up. (In some cases, special priming of the surface is necessary.)

2. Preparation of adhesive. May or may not be necessary, depending on the type.

3. Introduction of adhesive. Adhesive may be spread on one adherend surface or both or may be introduced as film.

4. Preliminary release of volatiles. While assembly is still open, enough volatile is released to develop proper tack for preliminary assembly; or as much volatile is released as is compatible with proper fusion and the wetting of the adherends when the assembly is closed. For optimum joint strength in exacting work, it may be necessary to control not only time but temperature and humidity as well.

5. Assembly. The several pieces of a multiple-part job are assembled.

6. Pressing or clamping. Pressure is applied to all joints to obtain a

continuous glue line of uniform thickness. Heating may or may not accompany pressing. Once the pressure has been applied, it must not be permitted to slacken until the adhesive reaches a substantial degree of set. This applies to all adhesives. Premature slackening of the pressure will cause the formation of vapor pockets and completely ruin the joint if the pressing is hot. In all cases, points of weakness, which greatly reduce the joint strength, will form. When setting has advanced to a certain stage, the pressure may be released.

7. *Conditioning.* The assembly is allowed to stand, often for several days, before it is fabricated or put into service. Usually, during this period the joint strength rises slowly until it reaches a maximum. This may be due to a slow continuation of the polymerization reaction in the case of space-polymerizing adhesives and to a release of localized internal stress, and hence the elimination of weak points, in all types (see also Sec. 818).

One and the same adhesive substance may be used at room temperature or at elevated temperatures. In other cases the same adhesive substance may be made for low-pressure or high-pressure manipulation. Highly practical and pragmatic considerations act as the determinants of these operating conditions, as may be gathered from the illustrations that follow.

Rather commonly, stronger bonding occurs at elevated temperatures even for room-temperature-setting adhesives. More groups at the adherend-adhesive interface receive the activation energy necessary for adsorption or reaction; adsorbed surface contaminants are more readily expelled or dissolved; volatiles are more thoroughly removed. As a consequence, adhesion and cohesion are both likely to be improved. In this instance the choice between operation at room temperature and at elevated temperature will depend on the following considerations.

1. Room-temperature operation eliminates the necessity for heated presses, which are themselves expensive. It also eliminates the cost and equipment entailed in heat generation. The joint strength obtained may be sufficient for the service requirements of the finished artifact.

2. Elevated-temperature operation results in stronger joints. It shortens the operating schedule by reducing the pressing time and often the conditioning period. Owing to these factors the production capacity is increased with very little change in over-all costs.

Dielectric heating so enormously decreases some bonding-cycle times that high-temperature operation has become almost mandatory in fields where room temperature had been the practice for years (Sec. 834).

By adding more or less strongly acid catalysts, space-polymerizing phenolic adhesives can be made suitable for pressing conditions ranging

from 2,000 psi and 300 F (high pressure and hot-setting) to 1 psi and 70 F (contact pressure and room-temperature-setting). The highly acid-catalyzed materials have the cost advantages arising from low pressure-low temperature operation, but the bond strengths, both adhesive and cohesive, are weaker. Pot life and open assembly times are short. Finally, the catalyst attacks metals and cellulose, often to a sufficient extent to reduce seriously the service life of the assembly (see Tables 8-9, page 354, and 16-1, page 664 and Secs. 852 and 1611 to 1613).

CHEMICAL TYPES OF ADHESIVES

1514. A wide variety of materials has been found suitable for adhesives. The early adhesives were of natural origin, *e.g.*, starches and animal glues. More recently, synthetic polymers have found extremely valuable applications. As in all other fields, research in adhesives is toward improved properties in particular directions so that many modern adhesives are synthesized for specific applications. Nevertheless, time-honored adhesives still combine low cost with strength adequate for many purposes. Although there are a few versatile adhesives that are generally applicable to the majority of surfaces, an adhesive having outstanding properties for all types of surfaces and bonding problems is a paradox unlikely of achievement.

A classification of adhesives based on chemical constitution and nature of chemical bonds is shown in Table 15-4.

TABLE 15-4. CHEMICAL CLASSIFICATION OF ADHESIVES

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- | | |
|--|---|
| 1. Low polarity | |
| a. Straight hydrocarbon. | Asphalts, hydrocarbon rubbers, hydrocarbon resins |
| b. Halogenated hydrocarbon. | Chlorine-bearing rubbers, chlorine-bearing vinyl polymers |
| 2. Medium polarity | |
| a. Nitrogen-, sulfur-, and silicon-containing. | Nitrile rubbers, thioplasts, sulfur, silicones |
| b. Oxygen-containing. | Shellac, rosin, waxes, phenolic resins, furan resins, acrylics, vinyl esters and acetals |
| 3. High polarity | |
| a. Oxygen-containing. | Starches, dextrans, gums, cellulose esters and ethers, polyesters, polyvinyl alcohol, silicates, magnesium oxychloride, litharge-glycerol |
| b. Amide and amine. | Protein (hide, bone, and blood glues, fish glues, casein, soybean), polyamides, urea resins, melamine resins |
-

Many commercial adhesives are compounded mixtures of the substances listed in Table 15-4 so that exact classification is not possible. An important example is the adhesives composed of phenolic resin and rubber, which bond to a wide variety of surfaces. Even adhesives with a single binder usually contain plasticizers, fillers, extenders, or other compounding ingredients.

ADHESIVES FOR WOOD

1515. In volume and importance, wood gluing overshadows all other adhesives applications. Furthermore, within this industry the greatest single application is in the manufacture of plywood.

Gluing in the wood industry is conveniently divided into primary and secondary bonding operations. Primary bonding covers the manufacture of large sheets, usually flat, *e.g.*, plywood. This is highly mechanized mass production. Secondary bonding covers the manufacture of finished articles such as furniture, building hardware, etc., which entails the assembling and gluing of several parts. This is largely a handicraft industry. For ordinary work, inexpensive glues such as cassava starch, soybean, albumin, and silicate are employed for primary bonding and animal glue for secondary bonding. When waterproofness and higher joint strength are essential, modified casein and space-polymerizing synthetic resins are used for both primary and secondary bonding.

Ordinary plywood is made by gluing veneers of seasoned wood at pressures of 250 psi or less (Sec. 941). Until 1930 this important structural material was bonded exclusively with animal and vegetable glues, all of which are the room-temperature-setting solvent-evaporation type. The pressing, or clamping, period was several hours or overnight. This plywood was all flat stock and could not meet the exacting demands of aircraft and certain engineering applications for two main reasons. (1) Destruction of the glue joint by microorganisms or chemical decomposition occurred, especially in moist atmospheres. (2) Delamination, particularly during the steaming and bending of flat stock into curved members, was common.

Though much plywood is still bonded with the older type glues, beginning with 1930 synthetic-resin adhesives, notably phenol-aldehydes and urea-aldehydes, were introduced in the wood industry with excellent results. They are introduced into the assembly as A-stage or B-stage molecules and polymerized to the C-stage *in situ*. Joints are readily attained with such strength that failure under stress takes place completely in the wood. These glues are not attacked by microorganisms, nor do they deteriorate chemically. The phenol-aldehydes are so resistant that after 4 years' exposure to extremely humid atmosphere no glue weakness develops even though the wood itself rots. Delamination does not occur even on steaming. The introduction of low-pressure bag molding (Sec. 852) made possible the production of pieces of any desired curvature free from internal stress.

The preparation of phenolic-resin adhesives is discussed in Sec. 1612. They are made with a high formaldehyde-to-phenol ratio and hence

contain many hydroxyl groups before they space-polymerize. There is considerable evidence that both low-stage urea and phenolic resins react with the hydroxyl groups of cellulose during their space polymerization, especially at elevated temperatures. Hence it is not surprising that the strongest joints are obtained by hot pressing. The relative merits of room-temperature-, warm-, and hot-setting phenolic-resin adhesives are listed in the preceding section.

For a long time it was not understood why ordinary wood adhesives gave poor results when used for bonding wood that had been previously heated. It is now recognized that hydroxyl groups of wood cellulose condense to form ether structures when heat is applied (Sec. 944). The poorer adhesion is thus readily explained.

ADHESIVES FOR METALS

1516. Owing to the dissimilarity between the metallic bond and other types of valence (Chap. 2) it is not surprising that good adhesives for metals, other than solders, are a comparatively recent development. The first great success in this field was the bonding of rubbers to metals cited in Sec. 1504, but the art has now progressed to the point where satisfactory adhesives are available for bonding metals to one another. The latter bonding offers advantages over soldering and similar operations for light-gauge metals and for aluminum and magnesium alloys. Furthermore, compared with rivets and similar fastenings, adhesive bonding is cheaper and often better (Sec. 1501).

Usually a successful adhesive contains valence bonds and a polarity similar to those of the adherends. This is not possible with the metals, so that adhesion must be attained in another manner. Metal adhesion depends upon the formation of a two-dimensional metal compound at the interface. For high-strength bonds this compound must be of primary-valence character, *e.g.*, the copper sulfide bond that forms when rubber is sulfur-vulcanized on brass. Bonds of lower strength can, of course, be effected by secondary-valence bridging.

The formation of a metal-adhesive bond is aptly illustrated in the case of polyvinyl acetate. If this adhesive is applied between metal adherends and the joint is effected via a cold-pressing technique, a joint strength of the order of 200 psi results. Probably the adhesion at the metal-adhesive interface depends upon the orientation of the carbonyl group toward the metal, a secondary-valence effect. By contrast, if hot pressing is employed, a joint strength of 2,000 psi or more is attained. Perhaps acetic acid released during heating forms a two-dimensional metal acetate, which is linked by hydrogen bonding to the acetate radicals in the adhesive. It appears to be universally true that high-strength

metal-adhesive joints require hot pressing, which induces chemical rather than physical adsorption.

On the above explanation one should expect adhesives for metals to contain groups that readily form metallic compounds. This is borne out in fact. Examples of successful metal adhesives are polyvinyl esters and acetals, polyesters, neoprene, chlorinated rubber, buta N, sulfur-vulcanized rubbers, and thiokol.

However, there is another requirement for metal adhesives. As explained earlier (Sec. 1508), the difference in coefficient of expansion between metals and organic polymers makes it imperative for metal adhesives to have elastomeric properties. Thus, phenol-aldehyde resins are not satisfactory metal adhesives despite the presence of the phenolic OH group, which has marked metal-combining properties, but excellent metal adhesives have been produced by using mixed phenolic resin-elastomer compounds. Similarly, casein-rubber mixtures are satisfactory adhesives for metals.

In joining a metal to a nonmetal adherend a single adhesive is frequently unsatisfactory for high-strength bonding, either because it is not possible to satisfy the bonding requirements of both adherends with one adhesive system, or because the nonmetal adherend will not withstand the temperature necessary for high-strength adhesion to the metal. For this reason, primer coats are commonly applied to the metal adherend beforehand. The primer coat is usually baked, thus giving excellent primary-valence adhesion to the metal.

Bonding between two nonporous adherends, whether one or both are metals, must be carried out in such fashion that substantially all volatiles have been expelled before the pressing step is reached if joints of high strength are desired (Sec. 1512).

BONDING OF ORGANIC PLASTICS

1517. The bonding of two thermoset adherends is usually effected with a space-polymerizing adhesive in order to preserve the strength, insolubility, and heat resistance of the adherends in the finished assembly. For bonding a thermoplast to a thermoset, the adhesive may be either thermoplastic or space-polymerizing. In the above systems, as well as in the bonding of wood and metals previously discussed, one or both of the adherends is insoluble and infusible. When this is the case, an adhesive *as such* must be introduced between the adherend layers and at some point in the bonding procedure this adhesive must be in an essentially liquid condition. Otherwise, intimate molecular contact with the insoluble adherends cannot be achieved, and proper adhesion between interfaces is impossible.

When the problem is to bond two thermoplastic soluble adherends to

one another, the situation changes radically. Obviously one has but to liquefy the two adherend surfaces to make bonding possible. This may be achieved by heat or solvent. No adhesive as such need be introduced. Such are the vagaries of language that the bonding of all plastics to one another, whether adhesive as such is required or not, is called *cementing*. Cementing in this sense is characterized by low pressures ranging from contact up to a maximum of perhaps 30 psi. Room temperature is very common although elevated temperatures are sometimes needed.

The cementing of two layers of identical thermoplast to one another is relatively simple and is conducted by any of three general methods.

1. The surfaces are plasticized with volatile solvent and clamped until bonding has resulted.

2. A solution of the thermoplast is made in an appropriate solvent, which is spread on the surfaces before closure. In both (1) and (2) very careful control of solvent release is usually essential to prevent warping, fogging, or undue disturbance of plasticizer concentration, if plasticizer is present.

3. The surfaces are plasticized by heat alone to a point where they will fuse under light pressure. This is sometimes called *welding*, sometimes *heat sealing*. Decomposition and serious loss of plasticizer must be avoided.

Heat for these operations may be applied by hot air, contact with hot metals, or dielectric devices. Seams can be joined between thin sheets of plastic or plastic-impregnated textile fabrics by passing them through a dielectric heater that looks somewhat like a sewing machine. This "sewing without thread" has initiated important technological advances.

The cementing of dissimilar thermoplasts is often more difficult since it may involve the solubility or thermal behavior of two binders and two or more plasticizers. In a few instances, cementing may be effected by solvent alone, but more usually an adhesive as such is required. An instance of the problems to be met is afforded by cellulose acetate and methyl methacrylate. The former contains considerable plasticizer, the latter none; and if migration of this plasticizer into the methacrylate takes place, crazing results. In this and similar cases the adhesive must not only be without plasticizer but must also "seal in" migratory plasticizers.

The cementing of a thermoset to a second plastic requires adhesive as such, in accordance with the discussion at the beginning of this section.

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See also Appendix A.

PARTICULAR TOPICS

See references under tables and figures of this chapter.

Wood Adhesives

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Bonding of Organic Plastics

SOCIETY OF THE PLASTICS INDUSTRY, Chap. 6 in "SPI Handbook," New York.

See also Appendix A-7.

CHAPTER 16

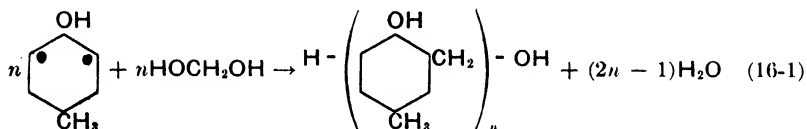
RESIN PRODUCT DEVELOPMENT: PHENOLIC RESINS

1600. It is the object of this chapter to show specifically how one synthetic resin system may be manipulated and developed into products of widely different character. The phenol-aldehydes are chosen for illustration since they may be made into outstandingly important resins suitable for molded and cast phenolics, laminated products, surface coatings, adhesives, and ion-exchange systems. Indeed, the development of the phenolic resins marked the true beginnings of the plastics industry as we know it today.

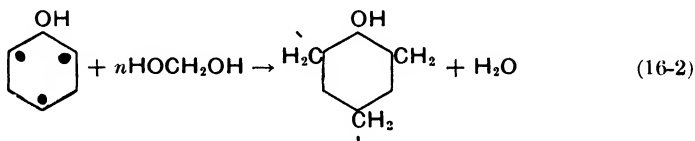
CHEMISTRY OF THE PHENOL-ALDEHYDES

1601. The reaction between phenols and aldehydes to form resinous products is general. Common phenol and formaldehyde are the monomers used most widely industrially, but cresols, xylenols, resorcinol, alkylated phenols, paraformaldehyde, hexamethylenetetramine ("hexa"), and furfural are also used. The resins do not exhibit well-defined x-ray patterns (Fig. 5-33, page 204), and the reactions are complicated, so that the early literature on the subject was badly obfuscated by the advancement of untenable theories on reaction mechanism and the postulation of highly improbable unsubstantiated molecular structures for the reaction products. Only some of the current concepts of the reactions based on what appears to be the best available experimental evidence are included below.

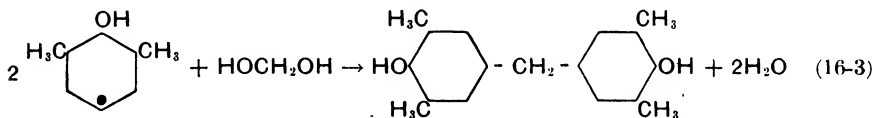
1602. General Features of the Phenol-Aldehyde Reaction. When a phenol reacts with an aldehyde, water is evolved but the phenolic hydroxyl group appears to be unaffected. Furthermore, when the one para and two ortho positions of the phenol are open, both linear and space polymerization can take place; when only two of these positions are open, only linear polymerization can occur; when but one is available no polymerization results. The basic reaction is thus condensation involving the aldehyde and ortho and para hydrogens of the phenol. Accordingly, *para*-cresol and formaldehyde form only linear polymers (it is helpful to represent the formaldehyde in its hydrated state as methylene glycol). The reaction may be represented as follows where each heavy dot marks the position of an active, functional hydrogen.



In common phenol, three functional positions are open, the system is tri-bifunctional, and space polymerization is possible.



3,5-xylenol has three functional positions open and forms space polymers, but 2,6-xylenol, with only one functional hydrogen, does not polymerize at all. Thus,



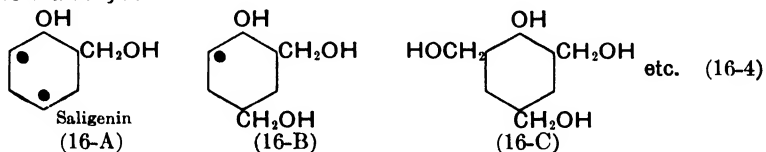
At the current writing, little precise information is available on the kinetics of the phenol-aldehyde reaction. The reaction is catalyzed by both acids and bases. Acids are the more powerful catalysts. Hydrochloric, sulfuric, sulfonic, and carboxylic acids have been successful. The most commonly used alkaline catalysts are sodium carbonate and ammonia, but many other bases are satisfactory. Nonfunctional substituent groups in the meta positions of phenol greatly increase the rate of condensation with formaldehyde, whereas the presence of these same groups in the para or ortho positions retard the reaction. Thus, the rate of condensation of various phenols with formaldehyde increases in the following order: 2,6-xylenol, *para*-cresol, 2,5-xylenol, 2,3,5-trimethylphenol, phenol, *meta*-cresol, 3,5-xylenol. For the addition reaction of these phenolic homologues with paraformaldehyde in the absence of water, the rate constant for 3,5-xylenol is about eight times as great as that of phenol, whereas that for 2,6-xylenol is only about one sixth that of phenol. When polyhydroxy phenols such as resorcinol are used in place of phenol, resinification is so rapid that no catalyst is required.

1603. Resinoid Formation. If proper control is exercised over reaction conditions and relative concentrations, common phenol and formaldehyde may be caused to condense with one another into small

nonpolymeric molecules before any large resinous molecules form. These small molecules are termed *resinoids* in this text. They are resin precursors in that they yield resins when caused to react further.

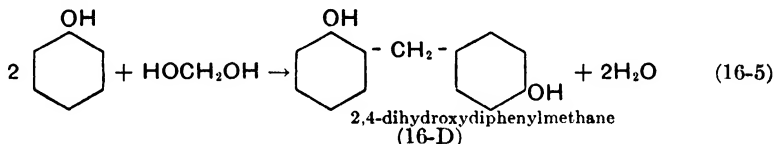
When equimolar amounts of phenol and formaldehyde are allowed to stand at room temperature in the presence of an alkaline catalyst, two monoalcohols are the main initial products but two dialcohols and perhaps even the trialcohol also form.

Phenol + formaldehyde \rightarrow



The formation of the di- and trialcoholic resinoids are favored by an aldehyde-phenol ratio greater than unity.

By contrast, when the above condensation is carried out in the presence of an acid catalyst, only dihydroxydiphenylmethanes can be isolated in the early stages of the reaction.



Probably saligenin forms but reacts immediately with a second molecule of phenol. The 4,4 and 2,4 isomers have been isolated, but not the 2,2 isomer. As would be expected, reaction (16-5) is favored by an aldehyde-phenol ratio less than unity.

The following important generalizations may be made. In the early stages of the phenol-formaldehyde reaction,

1. Alkaline catalysts and an aldehyde-phenol ratio greater than unity favor the introduction and accumulation of methylol groups on the benzene ring, *i.e.*, the reaction of each phenol molecule with one or more molecules of formaldehyde

2. Acid catalysts and an aldehyde-phenol ratio less than 1 favor the immediate reaction of each formaldehyde molecule with two phenol molecules so that the accumulation of methylol groups on a ring is minimized.

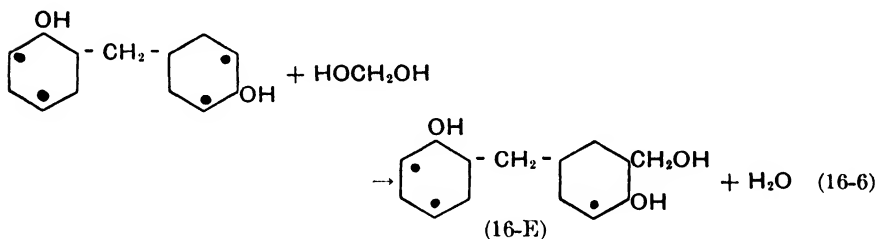
1604. Resin Formation. Regardless of the type of catalyst or resinoids formed in the early stages, increasing the reaction time or temperature leads ultimately to the formation of polymeric resinous products, but the type of polymer obtained varies with the conditions.

1. When formaldehyde is present in excess of phenol and the reaction is caused to proceed until resinification takes place, the resins formed are insoluble, infusible space polymers. These resins are essentially the same, regardless of the type of catalyst used.

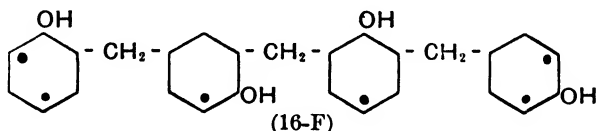
2. When phenol is present in excess, acid catalysis produces a permanently soluble, fusible linear resin called a *novolac*. On the other hand, an alkaline catalyst tends to yield an insoluble, infusible space polymer in spite of the presence of excess phenol.

Throughout this and the ensuing discussion it must be borne in mind that too great an excess of either reactant prevents the propagation of infinite networks or may prevent polymerization altogether in accordance with the principles discussed in Secs. 408 to 410. These results are in accord with the reactions previously described for resinoid formation at room temperature.

With acid catalysts, resin formation tends to proceed as follows: Dihydroxyphenylmethanes form in accordance with reaction (16-5). These react readily with additional formaldehyde to form monomethylol derivatives.

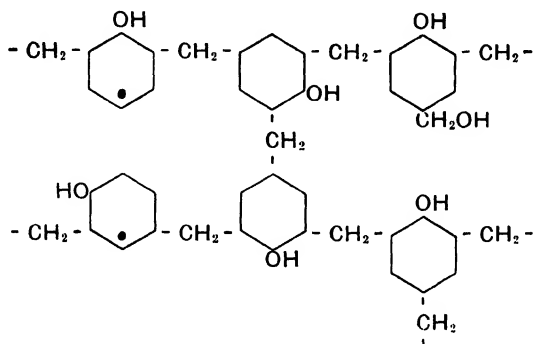


These immediately react with additional phenol. The repetition of this process results in chains of structure (16-F).

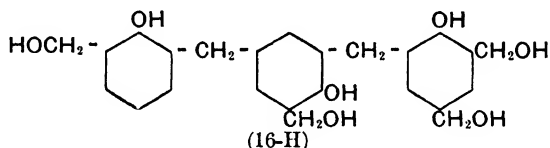


The formation of these chains involves the reaction of phenol and formaldehyde in essentially equimolar proportions, and the product is a permanently soluble and fusible novolac. Although the average molecular weight may be taken to as high as 1,500, the typical novolac contains an average of about six aromatic rings (D.P. = 6) and has a molecular weight of about 650. Since no methylol groups are available for cross-linkage, it will not harden to an infusible resin on heating. However,

if additional aldehyde is available and heat is applied, active hydrogen atoms on the novolac chains react with this aldehyde, leading to insoluble, infusible space polymers of structure (16-G).



With alkaline catalysts, the tendency is for phenol alcohols [Eq. (16-4)] to form initially. These are immediately capable of polymerization into chain molecules, which will tend to carry an appreciable number of methylol groups, as shown in structure (16-H).

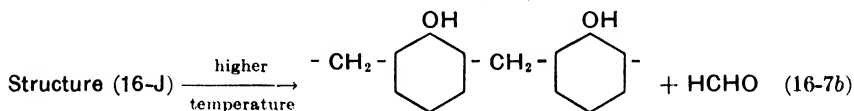
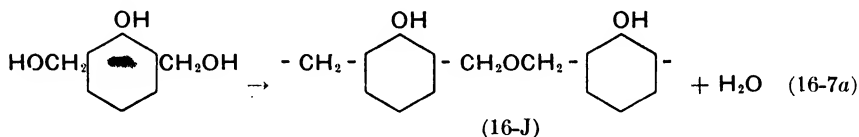


In this respect they differ from a novolac. Each methylol group represents a potential cross-link by which space polymers like structure (16-G) may form. However, if the reaction is stopped in its early stages as represented by structure (16-H), a soluble, fusible product is obtained that is called a *resole*, or *A-stage resin*. A typical resole contains about three aromatic rings and has a molecular weight around 350. If it is heated, it polymerizes to a somewhat larger, mildly cross-linked *resitol*, or *B-stage resin*, which is insoluble in alkali but partly or even completely soluble in acetone. This stage is still heat-fusible. Further heating results in a fully cured insoluble, infusible *resite*, or *C-stage resin* (Sec. 325). Backeland found that about one cross-link for every six aromatic rings is sufficient to produce a permanently infusible resin.

It is important to note that, with the exception of space-polymerized C-stage resins, the various phenolic resins of commerce are low polymers.

An A-stage resin may be converted to a novolac by heating with phenol. Conversely, a novolac may be converted to an A-stage resin by reaction with aldehyde.

The loss of formaldehyde is often observed in the transformation of phenolic resins to the final thermoset form during hot molding. This indicates that the conversion of phenol alcohols to phenolic resins may proceed via the formation of ether linkages. Thus, it has been reported that, when *para*-substituted dimethylol phenols are condensed by gentle heating, up to one molecule of water is split off without loss of formaldehyde, whereas, at the higher temperatures normally employed during hot compression molding, up to one molecule of formaldehyde is lost. Accordingly, the reactions presumed to occur are the following:



The formation of phenolic resins may be summarized as follows.

1. Under properly controlled conditions, phenol and formaldehyde may be caused to react in either acid or alkaline solutions in such ways that low-molecular-weight resinoids are obtained via the initial formation of either phenol alcohols or diarylmethanes.

2. These resinoids are capable of reacting further to give low-molecular-weight chain molecules, which are phenolic nuclei joined together by methylene or methylene ether linkages.

3. With acid catalysts the reaction tends to go at once to the ultimate product, whereas with alkaline catalysts it is easier to form intermediate products capable of further reaction.

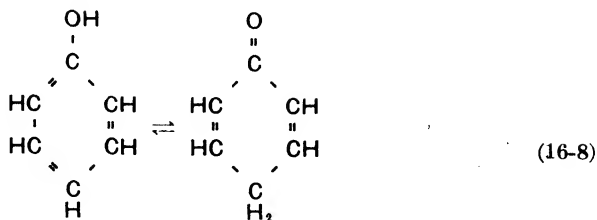
4. A proper excess of aldehyde must react with phenol if satisfactorily cured C-stage resins are to result.

1605. Color Characteristics. The following facts should be considered:

1. Pure phenol is colorless, but impure phenol turns pink and finally red.

2. When phenol comes in contact with iron salts, intensely red or purple compounds form.

3. A phenolic resin made from a *para*-substituted phenol develops less color than one made from the corresponding *ortho*-substituted phenol or phenol itself. Presumably blocking of the *para* position prevents rearrangement to chromophoric quinonoid structures, which may form as shown below so long as a *para* hydrogen is available (Sec. 1016).



4. Phenol forms deeply colored addition compounds with quinones and quinonoid compounds.

5. High temperature enhances the development of color bodies in phenolic resins.

Hot-molded and laminated phenolic resins are dark in color, and the artifacts made from them are relatively drab, red-browns and blacks prevailing. However, by using carefully purified reactants, preparing the resins in nickel or stainless-steel kettles, and avoiding high temperatures during polymerization to the C-stage, finished resins of a light straw color result, from which exceptionally beautiful, brightly colored artifacts may be produced.

THE MANUFACTURE OF COMMERCIAL PHENOLIC RESINS

1606. The chemical behaviors discussed in the previous sections afford the working basis for the manufacture of phenolic resins to suit various purposes. Accurate control over time, temperature, relative concentrations, and catalyst are all involved. These conditions may be varied over wide limits to attain the properties desired in the finished product. Furthermore, since common phenol, cresols, xylenols, resorcinol, etc., may be used singly or in combination, it is evident that a great range of resin characteristics is possible. Specific instances of how the system is manipulated to produce specific products are cited below.

1607. Resins for Hot Compression Molding. To be suitable as a plastic binder, a phenolic resin must be able eventually to set or cure to the C-stage. Consequently, no matter how made, the ultimate molecular ratio of aldehyde to phenol entering the mold must be somewhat greater than unity.

In making a resin for a hot-molding technique the problem is essentially as follows: Phenol and aldehyde must be reacted to some point short of the C-stage so that the resin will still exhibit plastic flow during molding. But the degree of polymerization must be such that subsequent cure to the C-stage will take place as rapidly as the particular molding method will permit. Otherwise molding cycles and production schedules will be unnecessarily prolonged. For hot compression molding (Secs. 812 ff.) a B-stage resin that will cure to the C-stage as rapidly as possible

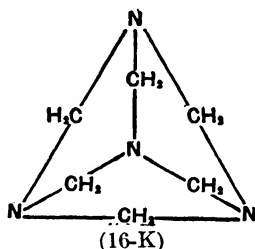
is called for. For transfer molding the curing characteristics must be such that the resin will not set before leaving the transfer pot and entering the mold. In other words, a long flow period is desirable. By varying the state of resinification of the polymer, the amount and character of the hardening agents, and the amount and character of the catalyst, it is possible to produce binders of different plasticity and curing properties suited to the several molding techniques and conditions. Strongly acid catalysts are ruled out for hot-molding resins since they would unduly corrode the mold.

Phenolic molding resins may be prepared by either a one-step or a two-step process. Although the former is somewhat cheaper, better control over the product is obtained by the latter process.

1608. *The One-step Process.* In the one-step process, about 1.4 moles of formaldehyde (sufficient to form an infusible C-stage resin) is heated at 185 to 205 F with 1 mole of phenol and a small weight percentage of catalyst in a steam-jacketed autoclave. The catalyst is often alkaline. The aldehyde is usually added as 37 per cent formalin solution. Since the batch is potentially heat-hardenable, control over the reaction is critical and must be carefully exercised both for uniformity of product and the avoidance of too much cross-linkage, which would result in a prematurely set resin difficult or impossible to manipulate. After the reaction has been permitted to proceed to a desired initial stage, the water is removed from the batch under vacuum and the dehydrated resin is then run out of the kettle. The reaction must be checked promptly, and it is essential that at this point the A-stage resin molecules contain sufficient methylol groups to ensure adequate cross-linkage during subsequent molding. The A-stage resin is next mixed with fillers, pigments, mold lubricants, and perhaps other compounding ingredients on heated rolls at temperatures around 212 F. During this operation further reaction takes place, bringing the polymer to a more viscous but still fusible B-stage. The mass is then cooled into sheets. The material is hard and brittle and is ground and sieved to a typical molding powder of uniform particle size.

1609. *The Two-step Process.* The salient feature of the two-step process is that the aldehyde is added in two portions. A soluble, fusible resin of the novolac type is first formed by reacting phenol with an amount of formaldehyde *insufficient* for the formation of an infusible product. Commonly about 0.8 mole for formaldehyde is used per mole of phenol. The kettling operation is conducted in a manner similar to that employed in the one-step process. Acid catalysts are most commonly employed. Since the novolac is incapable of cross-linkage and premature heat setting cannot take place, it will readily be understood why the process is easier

to control than the one-step process. After neutralization of the acid catalyst and dehydration of the batch the incorporation of compounding ingredients and other subsequent steps resemble the preparation of a one-step powder except that the additional aldehyde required for space polymerization to the C-stage must be incorporated into the mix in a convenient solid form such as paraformaldehyde or hexamethylenetetramine. The latter [structure (16-K)] is a particularly versatile and valuable agent.



At compression-molding temperatures (350 F) it acts as a flux, thus assisting in the actual shaping of the article, and it decomposes, supplying both ammonia, which serves as catalyst, and formaldehyde, required for cross-linkage. Furthermore, it does not liberate water (as does paraformaldehyde) so that there are less gassing and fewer undesirable effects on the molded artifact.

1610. Resins for Casting. To be suitable for casting (Secs. 837 *ff.*), a resin must be fluid enough to be poured into open casting molds. For this and other reasons, phenolic casting resins are considerably different from those used for hot molding. They were originally produced almost solely for the manufacture of highly colorable objects of art, jewelry, and other high-priced specialties. To attain this objective it is essential to avoid the formation of color bodies (Sec. 1605) and produce a resin that is nearly water-white. The procedure is as follows:

Specially purified phenol and formaldehyde are reacted by a one-step process employing alkaline catalyst in a stainless-steel or nickel-lined autoclave, the temperature being maintained at about 165 F. Typically, about 2.3 moles of formaldehyde (as formalin solution) is used per mole of phenol, and this high ratio of formaldehyde to phenol is one of the most striking differences between casting and molding resins. Owing to the large amount of formaldehyde and the alkaline catalyst, highly alcoholated, strongly hydrophilic molecules form. The conditions are adjusted so that the resin molecules remain at all times dispersed in the water. Precipitation or separation into a two-layer system is not permitted.

When the desired D.P. has been reached, the condensation is interrupted by neutralizing the alkaline catalyst with lactic acid. The

solution is subjected to vacuum dehydration at about 180 F until the water content has been reduced to about 5 to 10 per cent. The finished A-stage resin is a light straw color and has the consistency of honey when hot. The resin molecules are short chains carrying a large number of methylol groups. The water is an important constituent of this type of resin.

If it is desired to manufacture cast objects of optimum mechanical properties and colorability, the liquid resin is mixed with glycerol, coloring materials, and mold lubricant, poured into suitable open molds, and cured slowly to the C-stage by heating for 2 to 8 days at a low temperature, 158 to 176 F. As the curing proceeds, it is accompanied by the separation of the water of the resin into fine droplets, which remain entrapped in the hardened resin. The glycerol minimizes the scattering of light by these droplets, thus helping to maintain transparency.

The cast phenolics are unusual in respects other than color. They exhibit self-lubricating properties and exceptionally good machinability, as well as mechanical strengths without added filler that compare favorably with those of hot-molded phenolics *with* filler. These characteristics are attributable to two factors, the high degree of cross-linkage and the dispersed water droplets.

For obvious reasons, cast phenolics made as above are expensive. Rapid production, lower cost, and wider applicability may be attained by adding suitable amounts of hydrochloric acid or specially developed catalysts immediately before casting. This permits curing to the C-stage in 1 to 6 hr at room temperature instead of several days at elevated temperatures. Although this is accomplished at a considerable sacrifice in color stability, dimensional stability, and mechanical strengths (Table 16-1), the resulting products are still suitable for making many mechanical

TABLE 16-1. PROPERTIES OF HEAT-CURED AND ACID-CURED CAST PHENOLIC RESINS

Property	Heat-cured	Acid-cured
Tensile strength, psi.....	8,500-10,000	6,000
Compressive strength, psi.....	25,000-33,000	10,000
Flexural strength, psi.....	10,000-12,000	9,000

parts, tool handles, utensils, and even very large dies for producing light metal parts for airplanes and automobiles.

After-baking is advisable for all cast phenolics to case-harden them and improve their dimensional stability.

1611. Resins for Cloth and Paper Laminates. The procedures of high-pressure and low-pressure laminating are outlined in Secs. 849 ff.

A resin for high-pressure laminating of paper or fabric is prepared by a one-step process much the same as that used for making molding resins. The resin (A-stage) must be of such character that it is suitably soluble in alcohol or a mixture of alcohol and water so that the paper or fabric may be properly impregnated.

Resins prepared for low-pressure laminating must be different. Much low-pressure laminating is also conducted at low temperatures. Resins that will be satisfactory under these conditions may be made in various ways, as follows:

1. By a one-step process, highly alcoholated molecules of small size are produced. The small size ensures penetration of the filler and flow at the low temperature and pressure. The high aldehyde-to-phenol ratio induces a proper degree of cross-linkage and cure. Satisfactorily rapid cure at the low temperature may be obtained by adding strong acid catalyst just prior to use as in the case of the quick-curing casting resins previously discussed. However, since strong acid catalyzes the hydrolytic degradation of cellulose, limitations are imposed on this latter technique.

2. A novolac resin of low molecular weight is prepared. This is mixed with a large amount of hardener such as paraformaldehyde. Rapid cure is again obtained by adding a powerful catalyst.

3. A resin is made in which resorcinol is substituted for part or all of the phenol. Resorcinol-aldehyde resins set rapidly at room or moderately elevated temperatures without the addition of strong acids or bases, and thus deterioration of cellulosic fillers is avoided.

Depending on their operating characteristics, resins for low-pressure laminating are classified as room-temperature-, warm-, or hot-hardening as shown in Table 8-9, page 354.

1612. Phenolic-resin Adhesives for Wood. The gluing of wood has already been discussed in Secs. 941 and 1515, and the advantages of the space-polymerizing synthetic resins over the earlier glues have been mentioned. These synthetic glues must be applied as resinoids or low-stage resins and then cured to the C-stage *in situ* if good bonding is to result. Penetration of the resin into the wood is also conducive to high joint strength. Since adhesives must be spread, phenolic-resin adhesive molecules are small, with high formaldehyde-to-phenol ratios, so that they may be dissolved in water or alcohol to form solutions of low viscosity, good wetting power, and high penetrability. They may be room-temperature-, warm-, or hot-setting (Sec. 1513). The best cold-setting types are made with resorcinol.

Phenolic-resin adhesives are marketed in all physical forms, liquid, powder, split-batch, and film (Sec. 1510). In single-solution form, the

storage life is often short, and low storage temperatures are required. For this reason, split-batch forms are more common. The latter solutions contain novolac-type resin to which paraformaldehyde and catalyst are added immediately before use. Film has a long storage life and is easier and cleaner to handle than solutions.

1613. Phenolic Resins for Making Improved Woods. The resin in ordinary plywood is only a small fraction of the total weight of the material. The noteworthy improvements in mechanical properties that may be effected by saturating wood partly or completely with phenolic or urea resin were elaborated in the discussion of impreg and compreg (Sec. 943). If thick wood veneers are to be saturated to a considerable depth with resin by immersion in a solution, as in the production of impreg, it is essential to prepare very small and highly alcoholated polar molecules of resinoid rather than resin size. This is done by using a high formaldehyde-to-phenol ratio and arresting the reaction at a very early stage. It will be recalled that compreg is a product which, like impreg, contains a large synthetic-resin content but differs from the latter in that it has been densified by the application of heat and pressure in a press. In the manufacture of laminated and cross-bonded compreg, the required high resin content may be attained by applying phenolic resin in three different ways, *viz.*:

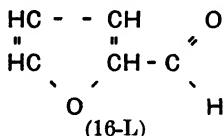
1. Impregnation of the veneers with a resinoid solution as in the production of impreg, followed by evaporation of the solvent and hot pressing

2. Interleaving of the veneers with sufficient film-type resin before pressing

3. Spreading sufficient liquid phenolic-resin glue between the veneers before pressing

Each of the three methods, involving its own type of resin, has advantages and disadvantages and yields products with somewhat different properties. The first method results in the material with the least springback (Sec. 942), but no method is superior in all respects. One experimental study yielded the results shown in Table 16-2.

1614. Phenol-Furfural Resins. Among the phenolic resins, those made from phenol and furfural are second in importance only to the phenol-formaldehydes. Besides the aldehyde groups, furfural possesses conjugated double bonds [structure (16-L)]. It is capable of polymeriza-



With phenol it therefore comprises a highly complex polyfunctional system.

It is believed that in its reactions with phenol it behaves like an ordinary saturated aldehyde in the early stages, where condensation results in soluble, fusible resins which are the counterpart of the phenol-formaldehyde products. However, in the final curing stages, the unsaturated furan ring appears to be active. Cross-linkage is accompanied by the disappearance of unsaturation. Apparently the conjugated bonds contribute toward an extensive system of cross-links, vinyl and Diels-Alder reactions (Secs. 429 *ff.*) occurring as well as condensation. This is confirmed by the full cure, dimensional stability, creep resistance, and good strength characteristics of the hot-molded products. The resins are darker in color than the phenol-formaldehydes. The usual fillers, plasticizers, etc., may be used in molding mixes.

TABLE 16-2. COMPARISON OF THREE METHODS OF COMPREG MANUFACTURE*†

Item	Impreg- nation process	Film- bonding process	Glue- spread- ing process
Simplicity and uniformity of production.....	3	1	2
Ease of compression.....	2	3	1‡
Dimensional stability:			
Water.....	1	3	2
Heat.....	3	1	2
Impact strength.....	3	1	2
Tensile and compressive strength, moduli of rupture and of elasticity in bending.....	2	1	3‡
Shearing stress parallel to grain:			
Perpendicular to laminations.....	2	1	3
Parallel to laminations.....	1	1	1
Machinability, glueability, paintability.....	3	1	2
Surface appearance.....	1	3	2

* KLEIN, L., H. GRINSFELDER, and S. D. BAILEY, *Ind. Eng. Chem.*, **36**, 252 (1944).

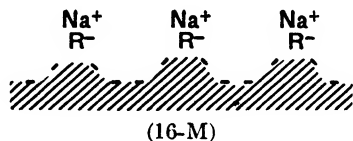
† 1 = best; 2 = intermediate; 3 = poorest.

‡ If a less alkaline resin were used, the ease of compression might have been somewhat less but the compressive strength, modulus of rupture, and modulus of elasticity might have been appreciably higher as indicated by data from other sources.

The greatest observable difference from phenol-formaldehyde resins, and the one of foremost industrial importance, is that there is no gradual transition from the fusible to the thermoset infusible state. Instead, this transition is very sharp. Linear fusible phenol-furfural resins may be kept "liquid" for long periods of time at temperatures slightly below their curing temperature; but once they are raised to the curing temperature,

cross-linkage and setting take place very rapidly. In other words, they have a long flow period, and in spite of their thermosetting character they are readily adaptable to extrusion, transfer, jet, and continuous injection molding (Chap. 8). For example, these resins may be held at temperatures at which they are sufficiently plastic for injection for as long as 45 min without setting. Furthermore, in hot compression molding, shorter cycles are possible than with phenol-formaldehydes since molding temperatures up to 400 F may be used without scorching of the binder. Mixed phenol-furfural-formaldehyde resins are widely employed for the entire gamut of molding, laminating, and varnish-making applications.

1615. Resins for Ion Exchange and Selective Sorption. Assume that there exists an ionic high-polymer molecule such that small positive cations like sodium ions are associated with a negatively charged anionic structure which is polymeric and of high molecular weight. The surface of this molecule is shown schematically in structure (16-M).



Let it now be assumed that this molecule is held in a fixed position in a moving stream of liquid containing in solution a salt whose cations are more strongly attracted to the polymeric anion than are the sodium ions; calcium ions with their higher charge density might be a case in point. The calcium ions will be attracted and tend to become fixed to the polymeric anion, and the displaced sodium ions will move downstream. This is a typical ion-exchange process. If a filter bed of proper thickness consisting of many molecules of structure (16-M) were constructed, hard water could be introduced on one side and soft water containing only sodium salts would emerge from the other. A zeolite water-softening unit is precisely such a structure. It consists of a space-polymeric anionic silicate framework of relatively open, molecularly porous structure associated with sodium ions (Sec. 520). The latter are displaced by calcium and magnesium ions when hard water is filtered through. Eventually the zeolite becomes loaded with these ions and loses its softening abilities. It is then regenerated by reversing the ion-exchange process by running through a sodium chloride solution so highly concentrated that the sodium-ion activity is sufficient to cause displacement of the hardness ions.

It will be readily understood that ion exchange is a very common phenomenon among both low- and high-molecular-weight materials. High polymers are particularly adaptable to the construction of operat-

able exchange filters for simple reasons. Their high molecular weight is accompanied by insolubility in the liquid medium being treated and the mechanical strength required for the construction of granular or massive filter beds.

General criteria may be postulated for an ideal ion-exchange material as follows:

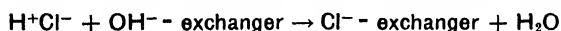
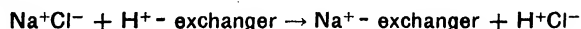
1. A large capacity for selective sorption of the material to be removed
2. Relatively open molecular structure, *i.e.*, "holes" into which the ions to be sorbed can readily penetrate
3. Large external as well as internal surface
4. Porosity on a macroscale sufficient to permit a proper rate of flow through the exchange bed
5. Sharp "break-through" point

Besides the above, regenerability may be highly desirable although not absolutely essential. If required, an additional criterion is

6. Inexpensive and ready regeneration

Synthetic space polymers are insoluble, mechanically rigid and easy to comminute. Their crystallinity is of a low order so that they incline toward a large internal surface. In the case of condensation polymers such as the phenolic and urea resins the water of condensation liberated as steam during hot curing imparts microporosity.

An extremely useful industrial development of ion-exchange technique is the production of demineralized water rivaling that of distilled water in purity. A two-part exchange filter is employed. In the first section there is a cation exchanger such as a phenolsulfonic acid space-polymerized with phenol and formaldehyde to form an interpolymers containing both phenolic hydroxyl and sulfonic acid groups. These ionize into mobile hydrogen ions and anions bound to the network. In the second section, an anion exchanger is used such as the copolymer of phenylenediamine, urea, and formaldehyde. This resin is basic. When water containing dissolved salts enters the exchange unit, the first section exchanges hydrogen ion for the metal ions and the second section removes the resulting acids.



There is evidence that some if not all of the anion exchangers operate simply by hydrogen bonding of the acid.



The cation exchanger is regenerated with acid, usually sulfuric acid, and the anion exchanger is regenerated with alkali, usually soda ash.

Synthetic resins and natural high polymers like clay may also be used

for the concentration or selective sorption of the constituents of a mixture in solution. The technique has been developed to a high degree and may be used as a method of analysis as well as separation. It is known as *chromatography*. The potential applications in pure and applied science are very great.

PHENOLIC SURFACE-COATING RESINS

Their excellent chemical resistance and water repellency early suggested the use of phenolic resins for surface coatings, but special products had to be developed before they proved truly successful in this field.

1616. Early Phenol-Formaldehyde Coatings. Ordinary novolac resins of low molecular weight may, like shellac, be dissolved in alcoholic solvents to form simple lacquers (unfortunately called "spirit varnishes," Sec. 1401). Indeed, this is the origin of the name novolac. A-stage phenol-formaldehyde resins may also be dissolved in surface-coating solvents. After application to the surface and evaporation of the solvent, heating results in a space-polymerized film. These products are therefore nonfatty varnish coatings of the baking type.

For most purposes, the coatings described above are not satisfactory because they are too brittle, adhere poorly, and darken considerably on aging since many of the para positions on the phenolic nuclei are open [Eq. (16-8)].

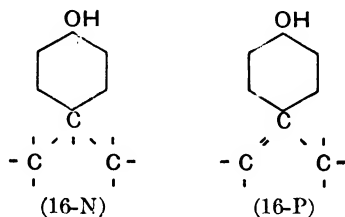
1617. Phenolic Resins for Oleoresinous Varnishes. Natural varnish gums and resins are expensive, and many arrive on the market in variable and uncertain amounts and quality since they are collected mainly by native labor in remote sections of the world. The urge to replace them with synthetic products has always been great. To that end, special phenolic resins have been developed since ordinary phenol-formaldehyde resins are insoluble in varnish oils.

To be suitable for oil varnishes, phenolic resins must meet the following general requirements: They must, of course, be soluble in oil. Furthermore, they must not be of the space-polymerizing type. Oleoresinous varnishes must be cooked to be of good quality (Sec. 1406); space-polymerizing phenolics cannot be introduced since they cause clotting under kettling conditions. Finally, they should not darken or discolor with age. These criteria may be met in several ways as described below.

1618. Straight Phenolic Varnish Resins. A *straight*, or 100 per cent, *phenolic varnish resin* is one that is soluble in varnish oil without having been previously combined chemically with natural resins, oils, or other synthetic resins.

By blocking the para or one of the ortho positions of common phenol with a group that does not react with formaldehyde, the phenol is reduced

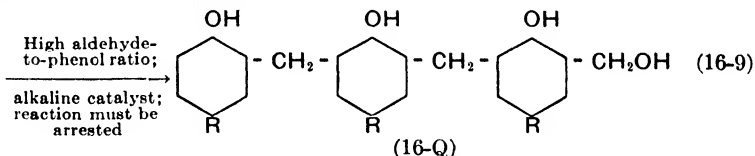
to bifunctionality and will form linear resins incapable of space polymerization. It was soon discovered that if the blocking group is branched oil solubility results. Finally, if the blocking group is introduced in the para position of the phenol, discoloration is minimized (Sec. 1605). Experiments reveal that other important advantages of para over ortho substitution are enhanced resistance to alkali and more rapid drying in the ultimate varnish film. Thus the fundamental criteria stated in the preceding section are met by using a phenol of structure (16-N) or (16-P). Examples are *para*-tertiary-butylphenol, *para*-tertiary-amylphenol,



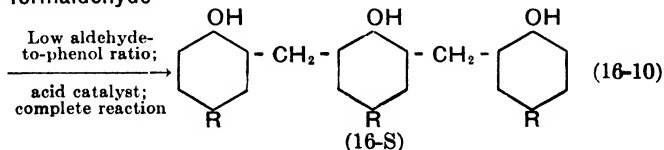
and *p*-phenylphenol. They are often prepared by reacting phenol with tertiary alcohols or olefins.

Upon condensing these phenols with formaldehyde, straight phenolic varnish resins of two distinct subtypes may be produced, depending, as usual, on the catalyst and the formaldehyde-to-phenol ratio.

Phenol derivative + formaldehyde



Phenol derivative + formaldehyde



In both types the molecular size is kept small as shown to maintain solubility.

Resins of structure (16-Q) are called *heat-hardenable*. Since they contain unreacted methylol groups, they are capable of straightforward condensation with one another to form longer molecules. When they are heated in a varnish mix, brisk foaming takes place at temperatures below 230 C, traceable principally to the moisture resulting from this reaction. This polymerization contributes toward the bodying of the

oil, a rapid rise in viscosity being noted. Both the brisk foaming and the rapid rise in viscosity make the kettling of the heat-hardenable resins somewhat difficult. Considerable skill and control are needed to prevent a sudden gelation of the batch (called *monkeying*), especially when tung oil is used.

Quite apart from the above reaction, several others occur that result in copolymerization of the resin and the drying oil, principally at temperatures above 230 C. These copolymerizations also contribute toward bodying of the varnish. One of these reactions is very probably a condensation involving alcohol groups of the resin with active hydrogens on the drying-oil molecules. The others involve unsaturated bonds since measurements of viscosity, gelation rates, and specific refraction show that the rate is increased by the degree of conjugation of the drying oil and also by the introduction of double bonds in the para position of the phenol of the resin. For example, comparable phenol-aldehyde resins were made from *p*-phenylphenol and *p*-cyclohexylphenol. In each case, 100 parts of the resin were mixed with 200 parts of tung oil, and the time to reach gelation at 250 C was measured. The gel time for the former was only 24 min, while that of the latter was 45 min. Although it is difficult to disentangle its individual features, evidence such as the above leaves little doubt that the reaction involves vinyl and modified Diels-Alder mechanisms.

The straight phenolic varnish resins represented by structure (16-S) are incapable of self-condensation. They are the so-called *non-heat-hardening* type. Their chemical combination with drying oils takes place mainly by the vinyl and Diels-Alder mechanisms cited above. The common practice of calling these resins "non-heat-reactive" is grossly misleading.

No foaming or sudden rise in viscosity such as that encountered with the heat-hardenable resins takes place. On the contrary, they retard polymerization in accord with the general fact that phenols are acidic and are oxidation inhibitors (Sec. 1404). This retarding action is of great value in the cooking of tung-oil varnishes. It eliminates the danger of monkeying and makes possible longer cooks at higher temperatures, resulting in very stable, nonskinning, nonwrinkling varnishes.

Both types of straight phenolic varnish resin, particularly when used in conjunction with tung oil, yield varnishes of exceptional merit. They impart to the film their general chemical inertness, high alkali resistance, and water repellency. Owing to the last, alternate swelling and shrinkage traceable to humidity are minimized, and one cause of pore and crack formation is eliminated. As noted in Chap. 14, one of the main causes for film failure is oxidation. Phenolic resins made from

properly chosen compounds such as *para*-phenylphenol, *para*-tertiary-butylphenol, and numerous similar phenols have a mild antioxidant effect that does not interfere with the rapid oxygen absorption involved during drying but does check the later, slow, continuous oxidation that normally decreases the life of the film. On the other hand, as previously noted in Sec. 1404, these resins are accelerators for nonoxidative polymerization. It is found that those which most actively accelerate polymerization during cooking likewise are most effective in promoting drying. The films are generally quick-drying, and those made with the heat-hardening type of resin are outstanding in this respect. Furthermore, for the several reasons outlined above, they are exceptionally durable.

The non-heat-hardening type of resins have the additional virtue of a phenomenal ability to prevent wrinkling in tung-oil varnish films even when considerable amounts of cobalt drier are used.

1619. Modified Phenolic Varnish Resins. A modified phenolic varnish resin is one that, before introduction into the varnish mix, has been reacted chemically with natural resin, synthetic resin, oil, or combinations of these.

Low-stage phenolic resins condense with the acids of various natural resins when the two are heated together. The resulting modified resin is oil-soluble. Most important among these is the reaction product with rosin [structure (14-B), page 600]. It is usually further modified by esterification with glycerol. This enhances the oil solubility, increases the molecular weight, and yields solutions of higher viscosity. Another way of arriving at essentially the same result is to modify the phenolic resin directly with ester gum. In either case the products are called *rosin-modified phenolics* and excel ester gum in their resistance to alkali, water, light, and oxidation. The melting point increases and the color grows darker with increase in the phenolic content. Phenolic resins may also be modified for special purposes by reaction with maleic anhydride and glycerol, drying and nondrying oils, and natural resins other than rosin, notably copal.

As an example of the molecular complexity often attained in surface coatings, the reader will find it instructive to consider the possible structures involved in the following succession of processes: A *para* substituted phenol is condensed with formaldehyde; the resulting resin is modified with rosin and glycerol; the product is further modified with maleic anhydride; the resulting resin is kettled with tung oil to form an oleo-resinous varnish, which then undergoes oxidative drying.

The chief advantage of the modified phenolic resins as a group is that they induce rapid drying of the varnish. They do not impart the same degree of durability and weather resistance as the straight phenolic types.

REFERENCES

GENERAL

CARSWELL, T. S., "Phenoplasts," Interscience Publishers, Inc., New York.

See also Appendix A.

PARTICULAR TOPICS

See references accompanying tables of this chapter.

Ion Exchange

MYERS, R. J., in "Advances in Colloid Science," Vol. 1, E. O. KRAEMER, editor, Interscience Publishers, Inc., New York.

APPENDIX A

GUIDE TO HIGH-POLYMER LITERATURE

A-1. In this text, references to the literature are to be found in three places, (1) accompanying the figures and tables throughout the book, (2) in the list of references at the end of each chapter, and (3) in this appendix.

The figures and tables have been selected wherever possible from articles or books of outstanding merit or importance. In themselves they serve as a guide mainly to reading on specific subjects. The function of the list of references at the end of each chapter is to provide a quick means of amplifying and complementing the subject matter of that particular chapter. Finally, the function of this appendix is to serve as a broad guide to extensive information on various aspects of the subject.

The objective of this scheme is to provide a guide for efficient auxiliary reading, which at the same time does not tend to divert the student's attention during study of the text itself. Indiscriminate reading in a subject which is as broad and has developed as rapidly as this one requires hundreds of hours, a luxury reserved only for the specialist.

BIBLIOGRAPHIES

A-2. The widely used abstracting and indexing services, such as (1) Chemical Abstracts, (2) Industrial Arts Index, and (3) Engineering Index, include high polymers. Abstract services specializing in the field are (4) Resins, Rubbers and Plastics (started in 1942), Interscience Publishers, Inc., New York; and (5) Natural and Synthetic Fibers (started in 1944), Interscience Publishers, Inc., New York.

Many of the publications listed below and at the ends of the chapters in the text contain excellent bibliographies.

BOOKS

The books listed below treat the subject matter of more than one chapter of this text. Books on particular topics are listed at the ends of the appropriate chapters in the text.

A-3. Books of Broad Scope. These books cover several phases of the subject of high polymers, such as the structure of molecules and their organic chemistry, polymerization, and physical chemistry of high-polymer systems.

STAUDINGER, H., "Die Hochmolekularen Organischen Verbindungen," Verlag, Julius Springer, Berlin (reprinted by Edwards Bros., Inc., Ann Arbor, Mich.).

ELLIS, C., "Chemistry of Synthetic Resins," 2 vols., Reinhold Publishing Corporation, New York.

MEYER, K. H., "Natural and Synthetic High Polymers," Interscience Publishers, Inc., New York.

OTT, E., editor, "Cellulose and Cellulose Derivatives," Interscience Publishers, Inc., New York.

BURK, R. E., and O. GRUMMITT, editors, "Frontiers in Chemistry," Vol. 1, "Chemistry of Large Molecules," Interscience Publishers, Inc., New York.

Conference on "High Polymers," *Ann. N.Y. Acad. Sci.*, **44**, 263-443 (1943).

TISS, S. B., editor, "Advancing Fronts in Chemistry," Vol. 1, "High Polymers," Reinhold Publishing Corporation, New York.

POWERS, P. O., "Synthetic Resins and Rubbers," John Wiley & Sons, Inc., New York.

FLECK, H. R., "Plastics," Chemical Publishing Company, Inc., Brooklyn.

Symposium on "Phenomena of Polymerization and Condensation," *Trans. Faraday Soc.*, **37**, 1-412 (1936).

Many books on organic chemistry give some consideration to high polymers. One book of treatise rather than ordinary textbook size and scope, which devotes considerable attention to this subject, is

GILMAN, H., editor, "Organic Chemistry," 2 vols., John Wiley & Sons, Inc., New York.

A-4. Chemistry and Kinetics of Polymerization

CAROTHERS, W. H., "Collected Works," Interscience Publishers, Inc., New York.

BURK, R. E., *et al.*, "Polymerization," Reinhold Publishing Corporation, New York.

MARK, H., and R. RAFF, "High Polymeric Reactions," Interscience Publishers, Inc., New York.

The following treatise includes catalysis in polymerization reactions:

BERKMAN, S., J. C. MORRELI, and G. EGLOFF, "Catalysis," Reinhold Publishing Corporation, New York.

A-5. Physical Chemistry of High-polymer Systems

MARK, H., "Physical Chemistry of High Polymeric Systems," Interscience Publishers, Inc., New York.

LEWIS, W. K., L. SQUIRES, and G. BROUGHTON, "Industrial Chemistry of Colloidal and Amorphous Materials," The Macmillan Company, New York.

"Advances in Colloid Science," Interscience Publishers, Inc., New York, KRAEMER, E. O., editor, Vol. 1; MARK, H., and G. S. WHITBY, editors, Vol. 2, "Rubbers."

Many books on physical and colloid chemistry give some consideration to high-polymeric systems. Books of treatise rather than ordinary textbook size and scope, which devote more than average space to this subject, are

WEISSBERGER, A., editor, "Physical Methods of Organic Chemistry," 2 vols., Interscience Publishers, Inc., New York.

ALEXANDER, J., editor, "Colloid Chemistry, Theoretical and Applied," 6 vols., Reinhold Publishing Corporation, New York.

A-6. Technology, Manufacture, and Applications. There are a large number of books in this category. A few of the recent and more comprehensive are listed here.

ALEXANDER, J., editor, "Colloid Chemistry," Vol. 6, "Synthetic Polymers and Plastics," Reinhold Publishing Corporation, New York.

AMERICAN SOCIETY FOR TESTING MATERIALS, "Symposium on Plastics," Philadelphia, 1944.

BARRON, H., "Modern Plastics," John Wiley & Sons, Inc., New York.

DELMONTE, J., "Plastics in Engineering," Penton Publishing Company, Cleveland.

MASON, J. P., and J. F. MANNING, "Technology of Plastics and Resins," D. Van Nostrand Company, Inc., New York.

- PLASTICS CATALOGUE CORP., "Modern Plastics Encyclopedia," New York.
- MORRELL, R. S., editor, "Synthetic Resins and Allied Plastics," Oxford University Press, New York.
- NAUTH, R., "Chemistry and Technology of Plastics," Reinhold Publishing Corporation, New York.
- RICHARDSON, H. M., and J. M. WILSON, "Fundamentals of Plastics," McGraw-Hill Book Company, Inc., New York.
- SASSO, J., "Plastics Handbook for Product Engineers," McGraw-Hill Book Company, Inc., New York.
- SIMONDS, H. R., and C. ELLIS, "Handbook of Plastics," D. Van Nostrand Company, Inc., New York.
- WAKEMAN, R. L., "Chemistry of Commercial Plastics," Reinhold Publishing Corporation, New York.
- WINDING, C. C., and R. I. HASCHE, "Plastics, Theory and Practice," McGraw-Hill Book Company, Inc., New York.
- YARSLEY, V. E., "Plastics Applied," London Trade Press, London.
- DEBELL, J. M., *et al.*, "German Plastics Practice," DeBell and Richardson, Springfield, Mass.
- CARSWELL, T. S., "Phenoplasts," Interscience Publishers, Inc., New York.
- SUTERMEISTER, E., and F. L. BROWNE, "Casein and Its Industrial Applications," Reinhold Publishing Corporation, New York.
- MATHEWS, J. M.; H. R. MAUERSBERGER, editor, "Textile Fibers," John Wiley & Sons, Inc., New York.
- BARRON, H., "Modern Synthetic Rubbers," D. Van Nostrand Company, Inc., New York.
- DAVIS, C. C., and J. T. BLAKE, "Chemistry and Technology of Rubber," Reinhold Publishing Corporation, New York.
- AMERICAN SOCIETY FOR TESTING MATERIALS, "Symposium on Applications of Synthetic Rubbers," Philadelphia, 1944.
- MATTIELLO, J. J., editor, "Protective and Decorative Coatings," 5 vols., John Wiley & Sons, Inc., New York.
- DELMONTE, J., "Technology of Adhesives," Reinhold Publishing Corporation, New York.

A-7. Manuals of Data and Processing Methods. There are a large number of books and pamphlets in this category. A few of the more comprehensive are listed here.

- BAKELITE CORP., "Molding Technique for Bakelite and Vinylite Plastics," New York.
- BOONTON MOLDING CO., "Ready Reference for Plastics," Boonton, N.J.
- CELANESE PLASTICS CORP., "Fabricating Methods for Lumarith, Celluloid, and Similar Thermoplastic Materials," New York.
- GOODRICH CHEMICAL CO., B. F., "Hycar Blue Book," Cleveland.
- LAUCKS, INC., I. F., "Technique of Plywood," Seattle.
- NATIONAL PAINT, VARNISH AND LACQUER ASS'N, "Paint Power," Washington, D.C.
- PLASTICS CATALOGUE CORP., "Modern Plastics Encyclopedia Charts," New York.
- PLASTICS MATERIALS MANUFACTURERS' ASS'N, "Technical Data on Plastics," Washington, D.C.
- SOCIETY OF THE PLASTICS INDUSTRY, "SPI Handbook," New York.
- VANDERBILT CO., R. T., "Vanderbilt Rubber Handbook," New York.

ZIFF-DAVIS PUBLISHING COMPANY, "Comparative Guide to Plastics Properties," Chicago.

The books listed in Secs. A-6 and A-8 contain information on processing methods used for high polymers as well as data on the properties of high polymers and their products.

Handbooks on chemistry and engineering contain data on the properties of high polymers and their products.

A-8. Test Methods and Laboratory Manuals

AMERICAN SOCIETY FOR TESTING MATERIALS, "ASTM Standards," Philadelphia.

Published separately and in various compilations, *e.g.*, Textile Materials; Paper and Paper Products; Plastics; Electrical Insulating Materials; Paint, Varnish and Related Products; Rubber Products.

D'ALELIO, G. F., "Experimental Plastics and Synthetic Resins," John Wiley & Sons, Inc., New York.

GARDNER, H. A., and G. G. SWARD, "Physical and Chemical Examination of Paints, Varnishes, Lacquers, and Colors," Gardner Laboratory, Bethesda, Md.

PERIODICALS IN ENGLISH

A-9. Research Periodicals. The following periodicals are noteworthy for the high caliber of articles reporting original research on polymerization and the organic and physical chemistry of high polymers and their products.

American Chemical Society Journal

Canadian Journal of Research

Chemical Reviews

Chemical Society Journal (London)

Faraday Society Transactions

Industrial and Engineering Chemistry

Institute of the Plastics Industry Transactions (London)

Journal of Applied Physics

Journal of Colloid Science

Journal of Organic Chemistry

Journal of Physical and Colloid Science

Journal of Polymer Science

Journal of Research of the National Bureau of Standards

Rubber Chemistry and Technology (mainly a reprint publication)

Textile Research Journal

A-10. Periodicals Covering Technology and Applications

American Dyestuff Reporter

American Leather Chemists' Association Journal

British Plastics

India Rubber World

Modern Plastics

Pacific Plastics

Paint, Oil and Chemical Review

Paper Trade Journal

Plastics

Rayon Textile Monthly

Rubber Age

Textile World

Periodicals in the general fields of chemical technology, engineering, materials, testing, etc., publish occasional articles on the applications and testing of high polymers and their products.

A-11. House Organs. There are a large number of publications in this category. Several of the more noteworthy are listed here.

American Cyanamid Plastics Newsfront

Bakelite Review

Celanese Plastics

DuPont Magazine

DuPont Plastics Bulletin

Durez Molder

Hercules Chemist

Interchemical Review

Monsanto Magazine

Paint Progress (New Jersey Zinc Co.)

Resinous Reporter (Resinous Products and Chemical Co.)

Rohm and Haas Reporter

Vanderbilt News

TRADE INFORMATION

A-12

SIMONDS, H. R., and J. V. SHERMAN, "Plastics Business," D. Van Nostrand Company Inc., New York.

Directories

British Plastics Year Book, Iliffe.

Modern Plastics Encyclopedia, Plastics Catalogue Corp., New York.

Rubber Red Book, Rubber Age, New York.

Thomas' Register of American Manufacturers, Plastics Section, Thomas Publishing Company, New York.

Trade Mark Directory, National Paint, Varnish and Lacquer Ass'n, Washington, D.C.

Plastics Magazine Annual Directory Issue, The Ziff-Davis Publishing Company, Chicago.

Chemical-industry directories contain trade information on the high-polymer industry.

Periodicals Specializing in Trade Information and Spot News

Oil, Paint and Drug Reporter

Industrial Plastics

Paint Industry Magazine

Paper Industry and Paper World

Plastics and Resins Industry

Plastics World

Textile Colorist and Converter

The periodicals listed in Sec. A-10 publish trade information. Periodicals in the general fields of chemical technology, materials, etc., also publish such information.

INTRODUCTION TO APPENDIXES B TO E

These appendixes are intended merely to *introduce* the reader to the factual data available on some of the more important high-polymeric materials. Obviously it is neither possible nor appropriate for a textbook to be encyclopedic in this respect. This is more properly the function of a handbook. Furthermore, a textbook cannot be up to the minute in this regard. This is the function of a yearbook. Appendix sections A-7 and A-8 contain references to such works.

The information included herewith is restricted to two groups of materials, (1) those used widely because of a combination of good properties and low cost and (2) those with one or more properties so outstanding that they are used despite cost. A.S.T.M. specifications are given wherever possible. In other cases, data were taken from the sources listed in the references accompanying the appendix tables. The specifications in these tables are not necessarily complete. For full coverage the original sources should be consulted.

It must be emphasized that tables such as these are useful only for preliminary or tentative selection. Final selection should not be based entirely on such "handbook" data, for five reasons. (1) The tests currently used for high polymers are often comparative rather than absolute. (2) Test methods have not been thoroughly standardized so that test values often vary considerably from one laboratory to another. (3) Different manufacturers of ostensibly the same material do not furnish identical products, owing to process variations. (4) A particular manufacturer can vary the structure and size of a basic polymer molecule, so that even if he ordinarily markets one grade he can supply other grades for special needs. (5) The development of new products is currently very rapid.

In the past, the number of kinds of polymer products available commercially was small, and each chemical type had its own fields of application, with little competition from others. Hence it was the custom in selecting a high polymer for a particular application to specify the chemical structure first and then to seek a particular source and mix to give the desired physical properties. Now, however, there are many polymers of different chemical types but similar engineering properties. Because of this growing availability and competition, in future the engineer will be able to specify strictly on the basis of performance (and price) rather than chemical structure. The numbering system of the Society of the Plastics Industry (SPI) (Appendix C) is a reflection of this significant trend. (Although the chemical structure is still included in the SPI classification, it is not a specification item.) The A.S.T.M. classification system for rubbers (Appendix D) is practically a complete step in this direction, although a distinction is still made between natural rubber and the synthetics.

APPENDIX B

PROPERTIES OF FIBERS¹

The following tables and figures in the running text contain comparative data and items of general interest in relation to fibers:

Table	Title	Page
9-1	Elastic moduli in tension for fibers and films	361
9-2	Influence of orientation on fiber tenacity.	365
9-4	Influence of length on tensile properties.....	366
9-5	Influence of diameter on tensile strength.....	366
9-6	Spirality and tensile strengths of natural cellulosic single fibers.....	368
9-7	Bundle strengths with varying degrees of twist.....	369
9-8	Influence of humidity on tensile behavior.....	370
9-9	Static-strength properties of various materials.....	376
11-2	Effect of moisture on swelling and strength of fiber materials.....	480
11-4	Modifying effects of acrylic resins on two fabrics.....	501
11-5	Effect of melamine resin on shrinkage of wool.....	502
 Figure		
7-10	Tensile stress-strain curves for various solids	269
9-6	Effect of rate of loading in tensile behavior of high polymers.....	372
9-7	Effect of temperature on mechanical properties of high polymers.....	373
11-2	Schematic features of fibers under the microscope.....	467
11-4	Load-elongation curves of fibers.....	474
11-6	Cyclic load-elongation curves of fibers.....	476
11-7	Relation between degree of elasticity and tenacity for rayon fibers.....	476
11-8	Relation between degree of resilience and elongation for fibers.....	477

Table B-1 gives properties of single fibers. Fibers normally reach the user only after manufacture into yarns, threads, cords, ropes, tapes, cloths, felts, mats, carpets, etc., in the almost endless ramifications that are introduced by varying such factors as twist, thread count, and finishing methods. Many of these products are sold not according to engineering requirements but according to aesthetic factors such as hand, drape, appearance, and style. It is thus not possible to present specifications for fiber products in the simple, brief manner employed for plastics and rubbers in Appendixes C and D.

Examples of engineering specifications for textiles are the following A.S.T.M. standards:

- D 122 Tire fabrics other than cord fabrics
- D 230 Cotton duck and Army duck

¹ See the Introduction to Appendixes B to E, p. 680.

- D 315 Asbestos tape for electrical purposes
 D 503 Bleached wide cotton sheeting
 D 504 Bleached cotton broadcloth
 D 505 Terry (Turkish) toweling
 D 576 All-wool, all-cotton, and wool-and-cotton blanketing
 D 625 Medium-weight cotton corduroy fabrics
 D 678 Finished, all-cotton, upholstery tapestries
 D 944 Mechanical roll felt

TABLE B-1. PROPERTIES

Fiber	Chemical nature	Common length of fiber, cm	Common width of fiber, mm	Specific gravity	Type
(1)	(2)	(3)	(4)	(5)	(6)
Cotton.....	Cellulose	1.5-5.6	0.012-0.025	1.5
Flax.....	Cellulose	20-240	0.013-0.025	1.5
Jute.....	Cellulose	150-360	0.0025-0.020	1.5
Hemp.....	Cellulose	100-300	0.015-0.060	1.5
Ramie.....	Cellulose	10-180	0.020-0.075	1.5
Viscose rayon.....	Cellulose regenerated from cellulose xanthate	As desired	As desired	1.5	Regular (R.T.) High tenacity (H.T.) Regular (R.T.)
Cuprammonium rayon	Cellulose regenerated from cuprammonium cellulose	As desired	As desired	1.5
Saponified acetate rayon.	Cellulose regenerated from orientated cellulose acetate	As desired	As desired	1.5	Medium tenacity (M.T.) High tenacity (H.T.)
Acetate rayon.....	Cellulose acetate, D.S. = 2-2.5	As desired	As desired	1.33	Regular (R.T.)
Silk.....	Silk fibroin (boiled off)	600-1,200 yd	0.010	1.3
Nylon.....	Polyhexamethylene adipamide	As desired	As desired	1.14	Regular (R.T.) High tenacity (H.T.)
Wool.....	Keratin	2.5-45	0.010-0.070	1.3
Casein.....	Formaldehyde-hardened casein	As desired	As desired	1.3
Polyvinyl chloride-acetate.	Vinyl chloride-acetate copolymer	As desired	As desired	1.35	Regular (R.T.) High tenacity (H.T.)
Saran.....	Vinylidene-vinyl chloride copolymer	As desired	As desired	1.7	Low tenacity (L.T.) High tenacity (H.T.)
Fiberglas.....	Special glass	As desired	As desired	2.54	0.0003 in. diameter
Stainless steel.....	18% Cr, 8% Ni	As desired	As desired	7.9	Cold-drawn wire

* 1 g/denier = 0.9 g/grex = (sp. gr. \times 9) kg/sq mm = (sp. gr. \times 12,800) psi. For most fibrous materials this value varies by as much as 50 to 300 per cent.

† For many fibrous materials, especially those which are moisture-sensitive, this value varies by as much as one-half to three times.

* Attacked by acids.

The data in Table B-1 are from several sources, notably

SCHMIDHAUSER, O., *Melliand Textilber.*, **17**, 905 (1936).

NICKERSON, R. F., in "Cellulose and Cellulose Derivatives," E. OTT, editor, Interscience Publishers, Inc., New York, 1943.

SMITH, H. D., *Proc. Am. Soc. Testing Materials*, **44**, 543 (1944).

PLASTICS CATALOGUE CORP., "Modern Plastics Encyclopedia Charts," New York, 1947.

OF SINGLE FIBERS

Standard moisture regain (70 F, 65% R.H.), %	Representative tensile strength* <i>P</i>				Representative elonga- tion at break† ϵ		Average stiffness <i>E_a</i> (<i>E_a</i> = <i>P</i> · <i>e</i>)		Toughness index <i>W_i</i> (<i>W_i</i> = <i>P</i> · <i>e</i> /2)		Other characteristics
	$\frac{g}{\text{denier}}$		psi × 10 ⁻³		%		$\frac{g}{\text{denier}}$	psi × 10 ⁻⁴	$\frac{g\text{-cm}}{\text{denier-cm}}$	$\frac{\text{in.-lb}}{\text{cu in.}}$	
	Dry	Wet	Dry	Wet	Dry	Wet					
(7)	(8)	(9)	(10)	(11)	(12)	(13)	(14)	(15)	(16)	(17)	(18)
8	4.0	4.5	77	86	7	7.5	57	110	0.14	2,700	a,b,d
12	6.0	6.3	115	121	1.8	2.2	333	642	0.05	1,000	a,b
14	3.5	67	...	1.3	269	515	0.02	440	a,b
12	6.0	115	...	1.7	353	675	0.05	1,000	a,b
..	6.0	7.0	115	134	2.5	2.5	240	460	0.08	1,400	a-b
13	2.0	1.0	38	19	16	24	13	24	0.16	3,000	} a,b,d
10	4.0	3.0	77	58	10	13	40	77	0.20	3,800	
12	2.0	1.1	38	21	13	21	15	29	0.13	2,500	a,b,d
11	5.6	4.0	108	77	6	7	93	180	0.17	3,200	} a,b,d,f
10	7.0	6.0	134	115	6	7	117	223	0.21	4,000	
6	1.4	0.9	24	15	25	30	6	10	0.18	3,000	a,b,e,f
10	4.0	3.4	67	57	16	26	25	42	0.32	5,400	a,b,e
4	4.6	4.0	67	58	22	26	21	30	0.51	7,400	} a
4	7.0	6.0	102	88	15	16	47	68	0.53	7,600	
17	1.4	1.2	23	20	35	45	4	7	0.25	4,000	a,b,d,e
13	0.8	0.35	13	6	30	100	3	4	0.12	2,000	a,b,d,e,f
0	2.3	2.3	40	40	25	25	9	16	0.29	5,000	} c,f
0	4.0	4.0	69	69	18	18	22	38	0.36	6,200	
0	0.7	0.7	15	15	20	20	4	8	0.07	1,500	} a(NH ₃),f
0	2.5	2.5	55	55	20	20	13	28	0.25	5,500	
0	6.5	6.5	210	210	2.5	2.5	260	840	0.08	2,600	a(HF,H ₃ PO ₄),h
0	2.0	2.0	200	200	25	25	8	80	0.25	25,000	a(HCl)

^b Attacked by alkalis.

^c Attacked by many organic solvents.

^d Attacked by mildew.

^e Attacked by moths.

^f Shrinks, melts, or loses strength on short-time exposure to 212 F.

APPENDIX C

PROPERTIES OF PLASTICS¹

The following tables and figures in other parts of the book contain comparative data and items of general interest in relation to plastics:

Table	Title	Page
7-1	Poisson's ratio for various materials.....	260
8-2	Effect of fillers on phenol-aldehyde plastics.....	314
8-3	Molded plastics and relation of fillers to applications.....	315
8-4	General properties of coloring materials used in plastics.....	320
8-5	Hot-compression-molding characteristics.....	328
8-6	Injection-molding characteristics.....	331
8-8	Properties of cold-molded materials.....	347
8-9	General types of resins used in low-pressure molding.....	354
9-1	Elastic moduli in tension for fibers and films.....	361
9-9	Static-strength properties of various materials.....	376
9-12	Tensile-creep data on various materials.....	389
9-16	Impact strengths of reinforced thermoset phenoplasts.....	414
9-17	Resilient energies on an equal-weight basis.....	415
9-18	Relationship between single-blow and repeated-blow impact strength..	416
9-19	Bending-fatigue data.....	425
10-1	Electrical insulating properties of materials.....	430
10-3	Thermal insulating properties of materials.....	454
10-4	Thermal expansion of materials.....	455
10-5	Optical properties of transparent plastics.....	459
E-1	Adhesion and compatibility.....	696
E-2	Plasticizers.....	700
E-3	Solvents.....	704
 Figure		
7-10	Tensile stress-strain curves for various solids.....	269
9-6	Effect of rate of loading in tensile behavior of high polymers.....	372
9-7	Effect of temperature on mechanical properties of high polymers.....	373
9-10 to 9-16	Creep data for plastics.....	384ff
9-19	Notch effect in various plastic products.....	392
9-21	Effects of fillers on properties of a binder-filler product.....	395
9-22, 9-23	Effects of molding conditions on properties of high polymers....	395-6
9-32	Variation of impact strength of a phenolic with temperature and filler.	415
9-34 to 9-38	Dynamic properties of plastics.....	420ff
10-1 to 10-18	Electrical properties of plastics.....	429ff

The N.E.M.A. uses letters to designate grades of laminated thermoset products, e.g., grade A is an asbestos-paper-base phenolic primarily intended for low-voltage

¹ See the Introduction to Appendixes B to E, p. 680.

applications where good resistance to heat, flame, and moisture is desired. The A.S.T.M. has adopted the NEMA grade letter designations (see A.S.T.M. D 709 Specifications for laminated thermosetting materials). Other plastics are described in A.S.T.M. standards by chemical name and type, *e.g.*, polystyrene, type 1. The type number indicates the application (type 1 is general purpose). For cellulosic molding compounds a grade designation is added to indicate the flow temperature (for grade H2, for example, it is 320 F).

For classifying plastics, the S.P.I. has adopted a detailed system based on physical properties. The SPI grade number consists of five digits; the first two indicate the minimum heat-distortion temperature, the next two the minimum impact strength, and the last the minimum tensile strength, all determined by specified A.S.T.M. methods. Thus, the polystyrene mentioned above is designated as SPI 17035, indicating 170 F heat-distortion temperature, 0.3 ft-lb per in. Izod impact strength, and 5,000 psi tensile strength. Suffix letters may be added to the SPI grade number to specify other properties in addition to those controlled by the grade number. Thus SPI 17035-Ob means that the polystyrene shall have the minimum light transmission specified by SPI, in this case 85 per cent. The chemical family is stated in the SPI classification but is not part of the specifications.

Since the range of properties is so great, it is convenient to subdivide plastic products into five groups as in the tables below: laminated, thermoset, thermoplast, cast, and nonrigid.

The data in the tables are from several sources, mainly

AMERICAN SOCIETY FOR TESTING MATERIALS, "Standards," Philadelphia, 1946, 1947.
PLASTICS CATALOGUE CORP., "Modern Plastics Encyclopedia Charts," New York., 1947.

PLASTICS MATERIALS MANUFACTURERS' ASSOCIATION, "Technical Data on Plastics," Washington, D.C., 1945.

SOCIETY OF THE PLASTICS INDUSTRY, "SPI Handbook," New York, 1947.

TABLE C-1. PROPERTIES OF LAMINATED THERMOSET SHEET

Material	A.S.T.M. standard	Heat-distortion temperature at 264 psi. (A.S.T.M. D 648), deg F, minimum	Maximum service temperature at no load, long time, deg F	Impact strength, I ₅₀ (A.S.T.M. D 256) ft.-lb./in. of notch, minimum		Tensile properties (A.S.T.M. D 229)		Flexural strength (A.S.T.M. D 229), psi, minimum	Compressive strength (A.S.T.M. D 229), psi, minimum	Specific gravity (A.S.T.M. D 792), maximum	Water absorption in 24 hr (A.S.T.M. D 570), 1/8 in. thick, % maximum	Effect of chemical reagents (A.S.T.M. D 543)		
				Flatwise 1/8 in. thick	Edgewise	Modulus, 10 ⁻⁶ psi, minimum	Ultimate strength, psi, minimum					Strong acids, nonoxidizing	Strong alkalis	Oxidizing acid
Melamine-formaldehyde, glass fabric base.	400	300	20	30,000	34,000	30,000	1.95	1.5	Decomposed	Attached	Decomposed
Phenolic, paper base ^a	D 709, grade X	280	250	1.3	0.50	0.4	10,000	20,000	20,000	1.40	3.3	Slight	Attached	Decomposed
Phenolic, fabric base.	D 709, grade C	280	250	3.2	2.0	0.35	7,500	16,000	35,000	1.36	2.5	Slight	Attached	Decomposed
Phenolic, fine-weave fabric base.	D 709, grade L	280	250	2.5	1.2	7,000	15,000	30,000	1.36	1.6	Slight	Attached	Decomposed
Phenolic, asbestos paper base.	D 709, grade A	280	300	1.8	0.80	5,000	10,000	30,000	1.8	0.95	Slight	Attached	Decomposed
Phenolic, asbestos fabric base.	D 709, grade A.A	280	350	3.5	3.0	8,000	16,000	35,000	1.8	0.95	Slight	Attached	Decomposed
Phenolic, glass fabric base.	400	450	5	1.0	11,000	20,000	42,000	1.8	Slight	Attached	Decomposed
Silicone, glass fabric base.	480	480	10	10,000	12,000	10,000	1.7	0.6	Slight	Attached	Slight
Vulcanised fibre, commercial grade.	D 710	175	0.8	6,000	12,000	20,000	1.20 minimum	65	Enbrittled	Swelled	Decomposed

^a See Table 9-13 for additional information.

TABLE C-2. PROPERTIES OF THERMOSETS, COMPRESSION- OR INJECTION-MOLDED

Material	A.S.T.M. standard	Heat-dis- tortion temper- ature at 264 psi (A.S.T.M. D 648), deg F, minimum	Maximum service temper- ature at no load, long time, deg F	Impact strength, Izod (A.S.T.M. D. 256) ft-lb/in. of notch, minimum	Tensile properties (A.S.T.M. D 638)			Flexural strength (A.S.T.M. D 790), psi, minimum	Compre- sive strength (A.S.T.M. D 695), psi, minimum	Specific gravity (A.S.T.M. D 792), maximum	Water absorption in 24 hr (A.S.T.M. D 570), % maximum	Effect of chemical reagents (A.S.T.M. D 543)		
					Modu- lus, \times 10 ⁻⁴ , mini- mum	Ultimate						Strong acids, nonoxid- izing	Strong alkalies	Oxidiz- ing acids
						Strength, psi, mini- mum	Elonga- tion, %, minimum							
Melamine-formaldehyde, cellu- lose filler. Phenolic resins, molding, no filler. Phenolic resins, wood-flour filler. Phenolic resins, high impact strength. Phenolic resins, heat resistant.. Urea-formaldehyde, cellulose filler.	D 704, type 1	300	260	0.20	6,000	9,000	25,000	1.55	1.8	Decom- posed	Attacked	Decom- posed
	D 700, type 1	230	250	0.30	0.75	7,000	Practi- cally nil	12,000	25,000	1.30	0.20	Slight	Attacked	Decom- posed
	D 700, type 2	260	300	0.24	1.05	6,500	0.4	9,000	22,000	1.45	0.80	Slight	Attacked	Decom- posed
	D 700, type 6	250	250	4.00	1.05	6,000	Practi- cally nil	9,000	15,000	1.45	1.75	Slight	Attacked	Decom- posed
	D 700, type 10	280	350	0.25	1.25	4,500	0.2	7,500	15,000	2.00	0.20	Slight	Attacked	Decom- posed
	D 705, grade 1	270	170	0.20	1.3	6,000	10,000	24,000	1.55	3.0	Decom- posed	Attacked	Decom- posed

TABLE C-3. PROPERTIES OF THERMOPLASTS, COMPRESSION- OR INJECTION-MOLDED

Material	A.S.T.M. standard	Heat-dis-tortion temper-ature at 264 psi (A.S.T.M. D 648), deg F, minimum	Maximum service temper-ature at no load, long time, deg F	Impact strength, Izod (A.S.T.M. D 256), ft-lb/in. of notch, minimum	Tensile properties (A.S.T.M. D 638)				Flexural strength (A.S.T.M. D 790), psi, minimum	Compres-sive strength (A.S.T.M. D 695), psi, minimum	Specific gravity (A.S.T.M. D 792), maximum	Water absorp-tion in 24 hr (A.S.T.M. D 570), % maximum	Effect of chemical reagents (A.S.T.M. D 548)		
					Modu-lus, psi X 10 ⁻⁴ , mini-mum	Ultimate		Decom-posed Softened					Decom-posed	Decom-posed	
						Strength, psi, mini-mum	Elonga-tion, % mini-mum								Strong acids, nonoxid-izing
Cellulose acetate, general pur-pose ^a	D 706, grade H2	144	140	0.7	0.18	4,600	15	8,500	20,000	1.34	4.4	Decom-posed	Decom-posed	Decom-posed	
Cellulose acetate butyrate, general purpose. ^b	D 707, grade H2	164	140	0.7	0.16	5,000	40	8,500	1.24	1.6	Decom-posed	Decom-posed	Decom-posed	
Ethyl cellulose, general purpose ^c	D 787, grade 1	140	150	2.5	5,500	10	6,000	11,000	1.14	1.7	Decom-posed	Slight	Decom-posed	
Fluoroethylene.....	D 788, type 1	144	400	4	0.06	2,000	300	2,000	1,700	2.3	0.00	None	None	None	
Methacrylate, general purpose, injection.	D 789	135	120	0.2	5,000	2	10,000	9,000	1.2	0.5	None	None	None	
Nylon.....	D 789	165	350	0.6	0.3	9,000	45	11,000	14,000	1.15	1.5	Attacked	None	Attacked	
Rubber, hard Herve, no filler ^d	175	0.5	0.3	9,000	4	15,000	8,000	1.14	0.2	None	None	Attacked	
Saran ^c	D 729	150	150	0.5	0.06	4,000	10	6,000	4,500	1.75	0.1	None	None	None	
												(except NH ₃)			
Styrene (polystyrene), general purpose.	D 703, type 1	169	150	0.30	0.4	5,500	2	8,000	14,000	1.07	0.10	None	None	Attacked	
Styrene (polystyrene), heat-resistant.	D 703, type 3	183	...	0.25	3,000	1	6,000	10,000	1.40	0.05	None	None	Attacked	
Vinyl chloride-acetate ^c	D 728, grade 1	125	130	0.25	7,500	...	12,000	9,000	1.35	0.15	None	None	Slight	
Vinyl formal.....		160	...	0.5	0.26	9,000	7	1.3	1.3	Attacked	None	Attacked	

For additional information see:

^a Fig. 2-13.^b Fig. 3-3.^c Table 13-4.^d Table 13-4.^e Table 8-7.^f Fig. 2-13.^g Fig. 3-3.^h Table 13-4.ⁱ Table 8-7.

TABLE C-4. PROPERTIES OF SHEETS AND CAST SHAPES

Material	A.S.T.M. standard	Heat-distortion temperature at 264 psi (A.S.T.M. D 648), deg F, minimum	Maximum service temperature at no load, long time, deg F	Impact strength, I-rod (A.S.T.M. D 256), ft-lb/in. of notch, minimum	Tensile properties (A.S.T.M. D 638)				Flexural strength (A.S.T.M. D 790), psi, minimum	Compressive strength (A.S.T.M. D 695), psi, minimum	Specific gravity (A.S.T.M. D 792), maximum	Water absorption in 24 hr (A.S.T.M. D 570), % maximum	Effect of chemical reagents (A.S.T.M. D 543)		
					Modulus, $\times 10^{-4}$ psi	Ultimate		Elongation, % minimum					Strong acids, nonoxidizing	Strong alkalis	Oxidizing acids
						Strength, psi, minimum									
Allyl resin.....	D 819	140	212	0.3	5,000	8,000	21,000	1.32	0.3	None	None	Attacked	
Casein.....	300	300	1.0	0.5	10,000	2.5	10,000	27,000	1.34	14	Decomposed	Decomposed	Decomposed	
Cellulose acetate, ^a 1/8-in.-thick sheet.	D 786, type I	131	140	1.4	0.25	4,000	25	6,000	20,000	1.34	4	Decomposed	Decomposed	Decomposed	
Cellulose nitrate, 1/4-in.-thick sheet.	D 701, type II	140	140	3.0	0.16	6,000	25	6,000	20,000	1.40	1.5	None	Decomposed	Attacked	
Methacrylate, 1/8-in.-thick sheet	D 702, type I	140	140	0.4	0.3	5,800	2	12,000	11,000	1.20	0.3	None	None	Attacked	
Phenolic resins, cast, mechanical grade, ^b	160	250	0.3	0.4	5,000	9,000	14,000	1.3	0.6	Slight	Attacked	Decomposed	
Vinyl chloride-acetate ^c	D 708, grade 1	125	130	0.3	8,000	13,000	10,000	1.36	0.15	None	None	Slight	

For additional information see:

^a Fig. 3-2.^b Table 16-1.^c Table 3-3; Figs. 2-5 and 2-6.

TABLE C-5. PROPERTIES OF NONRIGID PLASTICS

Material	A.S.T.M. standard	Brittle temperature (A.S.T.M. D 746), deg F, maximum	Maximum service temperature at no load, long time, deg F	Tear resistance (A.S.T.M. D 624), lb/in., minimum	Stiffness (A.S.T.M. D 747), psi, maximum	Tensile properties (A.S.T.M. D 412)		Specific gravity (A.S.T.M. D 792), maximum	Water absorption in 24 hr (A.S.T.M. D 570), %, maximum	Effect of chemical reagents (A.S.T.M. D 543)		
						Ultimate strength, psi, minimum	Elongation at rupture, % minimum			Strong acids, nonoxidizing	Strong alkalis	Oxidizing acids
Ethyl cellulose, ^a molding.....	D 743, grade 1	-13	140	180	2,000	1,400	80	1.14	1.3	Decomposed	Slight	Decomposed
Polythene (polyethylene).....	-50	200	440	13,000	1,200	100	0.93	0.03	None	None	None
Vinyl alcohol.....	200	2,000	300	1.26	> 30	Attacked	Dissolved	Attached
Vinyl butyral, thermoplastic.....	D 745, grade 3	-40	100	200	1,400	250	1.50	2.0	Attacked	Slight	Attached
Vinyl butyral, thermoset.....	D 745, grade 5	-31	140	200	1,800	200	1.50	2.0	Attacked	Slight	Attached
Vinyl chloride, ^b unfilled.....	D 744, grade 1	-4	150	550	2,750	2,600	300	1.38	0.30	None	Slight	None
Vinyl chloride-acetate, ^c unfilled.....	D 742, grade 1	0	150	500	5,500	3,000	250	1.24	0.20	None	None	Slight

For additional information see:

^a Fig. 2-15.^b Table 12-2.^c Table 3-3; Figs. 2-5 and 2-6.

APPENDIX D

PROPERTIES OF RUBBERS¹

The following tables and figures in other parts of the book contain comparative data and items of general interest in relation to rubbers:

Table	Title	Page
7-1	Poisson's ratio for various materials.....	260
9-17	Resilient energies on an equal-weight basis.....	415
10-1	Electrical insulating properties of materials.....	430
10-3	Thermal insulating properties of materials.....	454
12-2	Effects of vulcanization and carbon-black loading on elastomers.....	512
12-3	Comparative properties of elastomers.....	514
13-8	Effects of loading agents on mechanical properties of a vulcanizate.....	568
13-9	Properties of colloidal reinforcing carbon blacks.....	570
13-10	Vibration properties of various vulcanizates.....	582
C-5	Properties of nonrigid plastics.....	690
E-1	Adhesion and compatibility.....	696
E-2	Plasticizers.....	700
E-3	Solvents.....	704

Figure	Title	Page
7-10	Tensile stress-strain curves for various solids.....	269
9-7	Effect of temperature on mechanical properties of high polymers.....	373
13-9	Load-elongation curves of rubber vulcanizates.....	573
13-10	Tensile strength as a function of temperature for various vulcanizates..	574
13-14 to 13-25	Dynamic properties of rubber vulcanizates.....	576ff

The bulk of rubber is used for tires and tubes. Tires are made of carbon-black-loaded mixtures of natural rubber and buta S. Tubes are made of pure gum vulcanizates, either natural or butyl rubber. The desirable properties of tire and tube rubbers are indicated in Chaps. 12 and 13. Only Hevea and the buta rubbers are vulcanizable into hard rubbers, a comparatively minor application. Hard rubber is included in Appendix C, since it is a plastic rather than a rubber. The other important rubber products fall mainly into three use groups: rubbers for electrical wire and cable, those for mechanical applications, and cellular products (both open-cell and closed-cell).

The classification, specification, and selection of rubber products have gone very far in the direction of using performance rather than chemical nature as a basis. Although this does not mean that every chemical type of rubber can meet every application, it does imply that in most instances several chemical types can be successfully compounded to meet a particular requirement.

The A.S.T.M. jointly with the S.A.E. employs letters and numbers to designate two *types*, five *classes*, and various *grades* of rubber compounds to be used for mechanical purposes. The two types are R, carrying no specific requirement for oil and solvent

¹ See the Introduction to Appendixes B to E, p. 680.

resistance, and S, where resistance to the action of petroleum-base oils or other organic fluids is mandatory. There are two classes of type R, based on the composition of the elastomer: RN, in which the elastomer content is at least 50 per cent by volume of natural rubber; and RS, in which the elastomer content is at least 50 per cent by volume of synthetic rubber or rubberlike material. Type S compounds are divided into three classes, A, B, and C, based on the degree of oil resistance: SA, having maximum resistance; SB, having good resistance; and SC, having medium resistance. The grade numbers contain three digits; the first indicates the durometer hardness range, and the next two indicate the minimum tensile strength. Thus, RS 515 is the designation for a non-oil-resistant rubber compound with durometer hardness range of 50 ± 5 and a minimum tensile strength of 1,500 psi. In addition, the tables specify an ultimate elongation of 400 per cent for this product. An additional suffix number may be added if a higher ultimate elongation is required in the product. Thus RS 515-6 differs from RS 515 in that the minimum ultimate elongation must be 600 per cent. Finally, a suffix letter may be added to specify additional properties. Thus RS 515 B means

TABLE D-1. RUBBER COMPOUNDS FOR ELECTRICAL WIRE AND CABLE

Name of material	A.S.T.M. standard	Tensile properties (A.S.T.M. D 470)						
		Original			Strength after aging			
		Stress at 200 % elongation, psi, minimum	Ultimate strength, psi, minimum	Elongation at rupture, %, minimum	In air		In oxygen	
					Method	Psi, minimum	Method	Psi, minimum
Insulation Compounds								
Performance.....	D 353	300	1,200	400	a	1,020	f	900
Performance, synthetic.....	D 755	...	700	300	f	525
Polyvinyl.....	D 734	...	1,500	100	b	1,275		
Ozone-resistant.....	D 574	...	450	250	c	400	e	400
Heat-resisting.....	D 754	...	700	300	d	350	e	350
Sheath Compounds								
Rubber sheath compound.....	D 532	500	3,500	500	f	2,500
Polychloroprene.....	D 753	...	1,200	250	e	1,000	f	1,000
Polychloroprene, abrasion-resistant.....	D 752	500	1,800	300	c	1,600	f	1,600
Buta S.....	D 812	...	1,200	250	e	1,000
Buta S, abrasion-resistant.....	D 866	...	1,800	300	e	1,400

a Air at 70 C for 96 hr (A.S.T.M. D 573).

b Air at 100 C for 120 hr (A.S.T.M. D 573).

c Air at 70 C for 168 hr (A.S.T.M. D 573).

d Air, 80 psi, at 127 C for 20 hr (A.S.T.M. D 454).

e Oxygen, 300 psi, at 70 C for 48 hr (A.S.T.M. D 572).

f Oxygen, 300 psi, at 70 C for 96 hr (A.S.T.M. D 572).

g Oxygen, 300 psi, at 80 C for 168 hr (A.S.T.M. D 572).

that the rubber compound shall have the maximum compression set specified by the A.S.T.M., in this case 50 per cent, whereas suffix letter F designates a product passing the low-temperature brittleness test at -40°F .

The A.S.T.M. uses this same system of *letters* to designate types and classes of cellular rubber products, but in this group the *grade numbers* contain two digits and indicate the following:

Grades 10 to 19. *Sponge rubbers*. These are made by incorporating into the compound an inflating agent, such as sodium bicarbonate, that gives off a gas during vulcanization.

Grades 20 to 39. *Latex foam rubbers*. These are made from rubber latices. The cells are interconnecting. Numbers 20 to 29 are used for cored products, and numbers 30 to 39 for uncured products.

Grades 40 to 49. *Expanded rubbers*. These are made by dissolving in the compound a gas, such as nitrogen, under high pressure. The pressure is lowered during vulcanization. The cells formed are nonconnecting and gastight.

TABLE D-2. RUBBER COMPOUNDS FOR MECHANICAL APPLICATIONS*

Grade number	Duro-meter hardness number ± 5	Tensile properties		Change in volume after oil aging 70 hr (limits), %	Suffix-letter requirements	
		Ultimate strength, psi, minimum	Elonga-tion at rupture, %, minimum		Suffix A	Suffix E
					Change in ten-sile strength after oven aging 70 hr, %, maximum	Change in ten-sile strength after oil aging 70 hr, %, maximum
				158 F	158 F	158 F
RN 330	30	3,000	700	-25	
RN 535	50	3,500	600	-25	
RN 915	90	1,500	200	-25	
RS 320-7	30	2,000	700	-25	
RS 520	50	2,000	600	-25	
RS 625	60	2,500	450	-25	
RS 915	90	1,500	75	-25	
SA 302	30	200	500	-15 to +5	-20
SA 910	90	1,000	100	-3 to +3	-20
				212 F	212 F	212 F
SB 309	30	900	500	-15 to +25	-20	-20
SB 625	60	2,500	500	-5 to +25	-20	-20
SB 730	70	3,000	400	-5 to +25	-20	-20
SB 910	90	1,000	100	-5 to +25	-20	-20
SC 320	30	2,000	500	100 to 150	-15	-85
SC 530	50	3,000	500	80 to 130	-15	-70
SC 910	90	1,000	100	40 to 90	-15	-30

* These compounds are from A.S.T.M. D 735, rubber and synthetic rubber compounds for automotive and aeronautical applications. This standard does not include compounds for tires, inner tubes, sponge rubber, or hard rubber. (Only a few of the compounds included in the standard are listed here, the selection being made to illustrate the range available.)

TABLE D-3. CELLULAR RUBBER PRODUCTS*

Grade number	Compression deflection, 25% deflection, psi	Indentation, 25% deflection, psi	Change in volume after oil aging 22 hr at 158 F (limits), %
Sponge Rubbers			
RN 10 and RS 10	1		
RN 15 and RS 15	20.5		
SB 10	1	-25 to +10
SB 15	20.5	+10 to +60
SC 10 ⁴⁰⁻⁵⁰	1	-25 to +10
SC 15	20.5	+10 to +60
Latex Foam Rubbers (Cored)			
RN 21 and RS 21	0.19	
RN 28 and RS 28	2.37	
SC 21	0.19	+10 to +50
SC 28	2.37	+10 to +50
Latex Foam Rubbers (Uncored)			
RN 31 and RS 31	0.15	
RN 34 and RS 34	1.25	
SC 31	0.15	+10 to +50
SC 34	1.25	+10 to +50
Expanded Rubbers			
RN 41 and RS 41	3.5		
RN 43 and RS 43	11		

* These products are from A.S.T.M. D 798. Only a few of the products included in the standard are listed here, the selection being made to illustrate the range available.

APPENDIX E

ADHESION, COMPATIBILITY, AND SOLUBILITY¹

As indicated in Sec. 800, almost all high-polymer products are mixtures of 4 to 10 materials. Solubility and compatibility are thus of universal importance, while the related phenomenon of adhesion must be considered in connection with adhesives and coatings. A great variety of materials is used in mixes—high and low polymers, complex and simple molecules, both natural and synthetic. Terminology varies from one industry to another. Thus, a material may be called a plasticizer in the plastics trade and a softener in the rubber industry even though it serves precisely the same purpose in both.

This appendix is intended to furnish *generalized* information on adhesion, compatibility, and solubility. It is by no means sufficiently detailed or quantitative to serve as the basis for formulating highly complex mixes. Table E-1 shows adhesion and compatibility of high polymers with other high polymers and with certain waxes, resins, etc. Table E-2 deals with materials commonly listed as plasticizers, Table E-3 with solvents. In other words, the division of the tabulated information among these three tables is broadly in accordance with molecular weight (and volatility). Obviously, any such division is bound to be arbitrary. Thus, the main difference between "plasticizers" and "solvents" is one of volatility. The plasticizers in Table E-2 have boiling points of 230 C or higher, their vapor pressures at room conditions being 0.03 mm Hg or lower. However, many such materials are regarded as solvents when used in coatings because of their ready evaporation from thin films. To be useful as a coating plasticizer, a material should have a vapor pressure of less than 0.01 mm Hg, requiring a boiling point of 260 C or higher. By contrast, the solvents listed in Table E-3 boil at much lower temperatures.

For each material listed in the tables, compatibility or solubility with the more important high polymers is given. The behavior toward water, an outstandingly informative property, is also quoted. In Secs. 302*ff.*, it was shown that knowledge of the chemical composition and molecular structure of two compounds (*e.g.*, polymer and plasticizer) is of great aid in making qualitative predictions regarding compatibility. The accompanying tables substantiate this. It will be noted that the arrangement, both by rows and columns, is in accordance with polarity. This not only brings out the rule of "like attracts like" but also enables fairly reliable prediction of compatibility and adhesion even when data may be lacking in the tables.

The fact that a material is compatible or dissolves a particular high polymer does not necessarily mean that the mixture is satisfactory. Thus, even though compatible, butyl rubber must not be compounded with other rubbers or with unsaturated plasticizers and softeners, because they interfere with vulcanization.

Notes on Table E-1. As indicated in Chaps. 14 and 15, the formulation of coatings and adhesives is an involved process. Coatings and adhesives are purchased by chemical composition and brand name to a greater extent than other polymer products

¹ See the introduction to Appendixes B to E, p. 680.

		C, M	C, E	C, M	C	C, E		C, P	C, M	P	P	N, P				M		P	M
Halogen-containing																			
Neoprene	0.3	L	N, M	L	N	N, M		N	P	N, M	L, M	N, M	N			M		P	M
Rubber hydrochloride	0.1	L	L, M	L	L	C, E		C	M	P	C, E	N, M	N			M		P	M
Chlorinated Hevea rubber	0.00	P	P	P	P	P		P	P	P	P	P	P			M		P	M
Polyvinyl chloride																			
Saran																			
Polytetrafluoroethylene																			
Chlorinated paraffin																			
Medium polarity:																			
Nitrogen-, silicon-, and sulfur-containing																			
Buta N		P	C, M	C, P		C, M	C	C, P	C, P	E	C, E	N, E	E			E		M	E
Silicone resins																			
Silicone rubbers		P	P	P	P	P		P	P	P	P	P	P			P		P	P
Thioplast		N	C, M	L, P		C, P		C, E	C, P	P	P	N, P	P			M		P	M
Oxygen-containing																			
Polyvinyl ethers																			
Methyl isobutyl																			
Polyvinyl esters																			
Chloride-acetate	0.15	L	L, P	L, P	P	C, E	C, M		C, E	P	C, P	C, E	N, P	P		P		P	M
Acetate																			
Polyvinyl acetals																			
Formal	1.3																		
Butyral	2.0		E	C															
Acrylic resins																			
Polymethyl acrylate																			
Polymethyl methacrylate	0.5		C, M																
Poly- <i>n</i> -butyl methacrylate			C																
Furan resins																			
Phenolic resins																			
Phenol-formaldehyde	1.3		C, M	C, P	P	C, P	C, M	M											
Phenol-furfural	0.6		M	P	P	P	M												
Resorcinol-formaldehyde																			
Phenolic varnish resins																			
Straight																			
Modified																			
Shellac																			

* Key: C—compatible, L—limited compatibility, N—not compatible, E—excellent adhesion, M—moderate adhesion, P—poor adhesion.

TABLE E-1.* (Concluded)

[illegible]

[illegible]

* Key: C—compatible, L—limited compatibility, N—not compatible, E—excellent adhesion, M—moderate adhesion, P—poor adhesion.

Aromatic alcohol ethers: Ethylene glycol monobenzyl ether.....	0.4	N	N	N	N	N	N	N	N	N	L	C	C	C	benzyl Cello
Ketones															
Cyclic															
Terpene: Camphor.....	0.2										C	C	C	L	
Aromatic: Benzophenone.....	0	N	C	C	C	C	C	C	C	C	C	C	C	C	
Acids and hydroxyacids															
Aliphatic															
Acids: Oleic.....	0	C	C	C	C	C	C	C	C	C					
Hydroxy acids: Ricinoleic.....	0	C	C	C	C	C	C	C	C	C					
Esters, hydroxy esters, and oxyesters															
Aliphatic															
Containing only ester groups															
One ester group: Butyl stearate.....	0	N	C	C	C	C	L	N	N	N	N	C	C	N	N
Two ester groups															
Butyl sebacate.....	0	C	C	C	C	C	C	N	N	C	C	C	C	L	L
Propylene glycol stearate.....	0														
Butyl acetyl-ricinoleate.....	0	C	C	L	C	C	C	N	C	C	L	C	C	N	N
Ethylene glycol sebacate (low polymer).....	0														Baker P-6 Paraplex
Three ester groups															
Butyl carballylate.....	0										C	C	C	L	tripropionin
Glycerol propionate.....	0.3											C	C	C	
Four or more ester groups															
Pentaerythritol tetrabutylate.....	0											C	C	C	
Butyl acetyl-citrate.....	0	C	C	C	C	C	C	C	C	C	C	C	C	L	L
Glycerol diacetate acetyl-ricinoleate.....	0	C	C	L	C	C	C	C	C	C	L	C	C	N	Baker P-8 SOA
Sucrose octaacetate.....	0.09														
Containing ester and alcohol groups															
One ester group															
Butyl ricinoleate.....	0										C	C	C	N	
Propylene glycol monolaurate.....	0														
Glycerol monolaurate.....	0	C	C	C	C	C	C	C	C	C	C	C	C	C	
Propylene glycol monoricinoleate.....	0	C	C	C	C	C	C	C	C	C	C	C	C	C	
Glycerol monoricinoleate.....	0	C	C	C	C	C	C	C	C	C	C	C	C	C	
Two ester groups															
Glycerol diacetate.....	∞														diacetin
Propylene glycol ricinoleate.....	0											C	C	C	C
Butyl tartrate.....	0.5	C	C								C	C	C	C	C

[illegible]

*Key: C—compatible, L—limited compatibility, N—not compatible.

[illegible]

* Key: D—dissolves, L—limited solubility or latent solvent, N—not soluble.

because the complications introduced by the complexity of the mixes, the importance of specific chemical factors in adhesion, etc., often make purely physical tests an inadequate guide to selection. The references in Sec. A-8 contain listings of commercial products and their uses, with some information on their chemical composition.

The use of polymer mixtures, as distinct from copolymers, is increasing. Such mixtures, when compatible, usually have properties intermediate between those of the pure materials, with the additional factor of a mutual plasticizing effect. The data of Table E-1 may be of assistance in (1) selecting a chemical type of coating or adhesive for a particular problem, (2) selecting two or more polymer types for use in admixture, either in bulk as a plastic or rubber or as part of a coating or adhesive.

The following tables in other parts of the book contain comparative data and items of general interest in relation to these problems:

Table	Title	Page
3-4	Relation between properties and structural and chemical characteristics of high polymers.....	95
10-4	Thermal expansion of materials.....	455
15-2	Molecular-weight ranges for good adhesive properties.....	644
15-4	Chemical classification of adhesives.....	649

Notes on Tables E-2 and E-3. These tables give information on the behavior of *types* of plasticizers and solvents. Whenever possible, the data are given for a median member of a particular homologous series. Thus, in Table E-3, the solubilities stated for the aliphatic alcohols are those of butyl alcohol (4-carbon) rather than methyl alcohol (1-carbon) or cetyl alcohol (16-carbon). In such a series, the compounds become more hydrocarbonlike with increase in the number of carbon atoms. Hence, while methyl alcohol is a solvent for cellulose nitrate, butyl alcohol is a latent solvent and cetyl alcohol a nonsolvent. Similarly, in the plasticizers of Table E-2, the esters of the dibasic acids, *e.g.*, butyl sebacate, are listed as partly compatible with cellulose acetate, while actually the low members such as ethyl succinate are completely compatible. For the same reason, a type of compound may be listed differently in the two tables; *e.g.*, simple esters appear as nonsolvents for vinyl chloride in Table E-3 and as compatible with this polymer in Table E-2. These facts should be borne in mind in using the data.

The illustrative compounds chosen are not necessarily the most widely used representatives of the particular chemical types. Extensive listings of commercially available plasticizers and solvents are found in the references cited in Sec. A-7.

The following tables and figures in other parts of the book contain comparative data and items of general interest in relation to plasticization and solubility of high polymers:

Table	Title	Page
14-4	Lacquer-solvent combinations.....	611

Fig.		
3-3	Plasticizer content and physical properties.....	83
3-4	Effect of plasticizer content and temperature on properties of high polymers	83
6-9	Solubility of <i>n</i> -paraffins in aromatic hydrocarbons.....	233
9-31	Effect of added plasticizer on toughness and impact strength.....	415
14-1	Effect of solvent on viscosity-concentration curve.....	606

REFERENCES

The data in these tables are largely from manufacturers' publications. Other sources include the following:

INDIA RUBBER WORLD, "Compounding Ingredients for Rubber," New York, 1947.

MATTIELLO, J. J., editor, "Protective and Decorative Coatings," Vols. 1 and 3, John Wiley & Sons, Inc., New York.

PLASTICS CATALOGUE CORP., "Modern Plastics Encyclopedia Charts," New York, 1947.

PLASTICS MATERIALS MANUFACTURERS' ASSOCIATION, "Technical Data on Plastics," Washington, D.C., 1945.

SARBACH, D. V., and B. S. GARVEY, JR., *India Rubber World*, 115, 793 (1947).

APPENDIX F

CHEMICAL FORMULAS AND NAMES OF HIGH POLYMERS

The body of this book contains structural formulas of most of the widely used high polymers. These are not repeated here, for the treatment within the text covers such variations as copolymerization, degree of cross linking, etc. It is a misleading simplification to represent the structure of most high polymers by one simple mer.

Wherever possible, trade names have been avoided in the text for several reasons.

1. Their primary purpose is to identify a particular company's products rather than to be descriptive of a chemical entity. For this reason trade names are often applied to several products of a company, although they may differ widely in chemical nature. For example, Textolite is applied by the General Electric Company to both their molded and laminated products, which may be phenol-formaldehyde, silicone, polystyrene, etc.

2. Many high polymers are made by more than one company, each using different trade names for similar materials. For example, cellulose acetate may appear as Chemaco CA, Fibestos, Hercules Flake CA, Lumarith, Nixon CA, Plastacele, or Tenite I.

3. Although most companies indicate different types of a particular high polymer by numbers or letters, some employ different trade names. For example, the Monsanto Chemical Company uses Cerex, Lustron, and Styramic to indicate three different types of styrene polymers.

4. The meanings of trade names are not stable. They are withdrawn, broadened as to application, or otherwise changed with time. Thus, for many years Bakelite meant a phenolic resin, and many persons today use "bakelite" as a common name for phenolic products. However, the Bakelite Corporation has never allowed this term to become generic, and the trade name Bakelite now covers several radically different polymers made by this organization, *e.g.*, Bakelite polystyrene and Bakelite polyester resin.

The following listing of trade names is therefore given for what it is worth at the current writing:

Chemical family, common or generic name (none of these is protected by trade-mark)	Chemical nature or polymerization type	Mer	Representative trade names*
Acrylic (see also Methacrylate)	Vinyl addition	Secs. 414 <i>ff.</i>	Acryloid
Alkyd (see Polyester)			
Allyl (see also Polyester-vinyl)	Vinyl addition	Linear $\begin{array}{c} \text{—CH—CH}_2\text{—} \\ \\ \text{CH}_2\text{OR}' \end{array}$ Cross-linked $\begin{array}{c} \text{—CH—CH}_2\text{—} \\ \\ \text{CH}_2\text{R} \\ \\ \text{O} \\ \\ \text{CH}_2\text{R} \\ \\ \text{—CH—CH}_2\text{—} \end{array}$	CR resins, Kriston
Aniline-formaldehyde	Amine-aldehyde condensation	$\begin{array}{c} \text{—N—CH}_2\text{—} \\ \\ \text{C}_6\text{H}_5 \end{array}$	Cibanite, Dilectene
Azlon (applied only to artificial and synthetic polyamide fibers)	Polyamide	Eq. (2-9)	
Benzyl cellulose	Cellulose ether	Sec. 442	
Butadiene (see also GR and buta rubbers)	Diene addition	Eq. (1-16), Secs. 430 <i>ff.</i>	
Buta N	Diene addition	Secs. 430 <i>ff.</i>	Butaprene N, Chemigum N, Hycar OR
Buta S	Diene addition	Eq. (1-17), Secs. 430 <i>ff.</i>	Butaprene S, Hycar OS
Butyl rubber is a copolymer of isobutene and isoprene			
Carboxymethyl cellulose	Cellulose derivative	$\begin{array}{c} \text{OH} \quad \text{OH} \\ \quad \\ \text{—CH—CH—} \\ \quad \\ \text{—CH—CH—O—} \\ \quad \\ \text{CH—O—} \\ \\ \text{H}_2\text{COCH}_2\text{COONa} \end{array}$	CMC
Casein	Natural polyamide	Table 4-10, Eq. (11-6)	Ameroid, Galalith, Aralac (fiber)
Cellophane (applied only to film)	Regenerated cellulose	Secs. 435 <i>ff.</i>	
Cellulose	Cellulose	Secs. 524 <i>ff.</i>	
Cellulose acetate	Cellulose ester	Table 2-11, Sec. 441	Lumarith, Plastacele, Tenite I

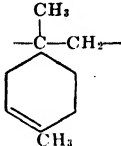
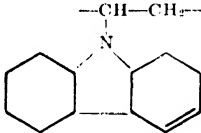
*For footnotes see p. 714.

Chemical family, common or generic name (none of these is protected by trade-mark)	Chemical nature or polymerization type	Mer	Representative trade names*
Cellulose acetate-butyrate	Cellulose ester	Sec. 441	Tenite II
Cellulose acetate-propionate	Cellulose ester	Sec. 441	Tenite III
Cellulose nitrate	Cellulose ester	Sec. 441	Celluloid, Nitron, Pyralin
Cellulose propionate	Cellulose ester	Sec. 441	Forticel
Chlorinated (Hevea) rubber	Hevea-rubber derivative	$\begin{array}{c} \text{CH}_3 \\ \\ -\text{CH}_2-\text{C}-\text{Cl}-\text{Cl}-\text{CH}_2- \end{array}$	Parlon
Chloroprene (see Neoprene)			
Coal-tar resins (see Coumarone, Indene)	Vinyl addition	Polymers and copolymers of coumarone and indene	Cumar, Nevindene, Piccoumaron
Cold-molded	Various types	Sec. 841	
Coumarone (see Coal-tar resins)	Vinyl addition	$\begin{array}{c} -\text{CH}-\text{CH}- \\ \quad \\ \text{C}_6\text{H}_4 \end{array}$	
Cresol-aldehyde (see Phenolic resins)			
Cyclized rubbers	Derivatives of Hevea and buta rubbers		Marbon, Pliolite, Thermoprene
Ethyl cellulose	Cellulose ether	Sec. 442	Celcon, Ethocel
Ethylene (see Polythene)			
Ethylene glycol	Polyether	Eq. 4-35	Carbowax
Furan resins: Furfural	Vinyl addition	$\begin{array}{c} -\text{CH}-\text{CH}- \\ \quad \\ \text{O} \\ \\ \text{CH}=\text{C}-\text{CHO} \end{array}$	Duralon, Furetone, Plaspreg
Furfuryl alcohol (Both addition and condensation probably occur in the formation of furan resins)	Condensation	$\begin{array}{c} \text{HC}-\text{CH} \\ \quad \\ -\text{C} \quad \text{C}-\text{CH}_2- \\ \quad \\ \text{O} \end{array}$	

Chemical family, common or generic name (none of these is protected by trade-mark)	Chemical nature or polymerization type	Mer	Representative trade names*
GR-A (see Buta N) GR-I (see Isobutene) GR-M (see Neoprene) GR-S (see Buta S)			
Hydroxyethyl cellulose	Cellulose derivative	$ \begin{array}{c} \text{OH} \quad \text{OCH}_2\text{CH}_2\text{OH} \\ \quad \\ \text{CH} - \text{CH} \\ \quad \\ -\text{CH} \quad \text{CH}-\text{O}- \\ \quad \\ \text{CH} - \text{O} \quad \text{H}_2\text{COCH}_2\text{CH}_2\text{OH} \end{array} $	Cellosize
Indene (see Coal-tar resins)	Vinyl addition	$ \begin{array}{c} -\text{CH} - \text{CH}- \\ \quad \\ \text{CH}_2 \quad \\ \\ \text{C}_6\text{H}_5 \end{array} $	
Isobutene (Isobutylene)	Vinyl addition	Table 2-11, Secs. 414 <i>ff.</i>	Vistanex, Synthetic 100
Melamine-formaldehyde	Amine-aldehyde condensation	Sec. 1439	Melmac, Resimene, Uformite
Methacrylate	Vinyl addition	Secs. 414 <i>ff.</i>	Lucite, Plexiglas
Methyl cellulose	Cellulose ether	Secs. 442	Methocel
Neoprene†	Diene addition	Table 2-11, Secs. 430 <i>ff.</i>	
Nitrile rubber (see Buta N)			
Nylon†	Polyamide	Table 1-1, Eq. (2-9)	
Parchmentized paper	Sulfuric-acid-treated cellulose	Sec. 436	
Phenol-formaldehyde (see Phenolic resins)			
Phenol-furfural (see Phenolic resins)			Durite
Phenolic resins	Phenol-aldehyde condensation	Chap. 16	Catalin, Bekacite, Durez, Resinox, and many others
Phenolsulfonic-aldehyde (see Phenolic resins)			Amberlite, Dowex
Polyester (see also Polyester-vinyl)	Phthalic resin	Sec. 1432	Beckosol, Duraplex Glyptal, Rezyl.
	Maleic resin	Eq. (4-43), Sec. 1433	Beckacite, Carbic, Petrex, Teglac.
	High aliphatic polyester	Table 1-2	Paraplex

*For footnotes see p. 714.

Chemical family, common or generic name (none of these is protected by trade-mark)	Chemical nature or polymerization type	Mer	Representative trade names*
Polyester-vinyl	Addition and condensation	Reaction products of intermediates such as shown in structure (1-B) and Eq. (4-43)	MR resins, Selectron, Thalid, Vibrin,
Polythene†	Vinyl addition	Table 1-1, Secs. 414ff.	
Pyroxylin (see Cellulose nitrate)			
Rayon, acetate (see Cellulose acetate)			Celanese rayon, Fortisan, Teca
Rayon, cuprammonium	Regenerated cuprammonium cellulose	Sec. 436	Bemberg
Rayon, viscose	Regenerated xanthate cellulose	Sec. 443	
Resorcinol-formaldehyde (see Phenolic resins)			Lauxite, Penacolite
Rubber, Hevea	Natural hydrocarbon polymer	Structure (12-B), Sec. 1215	
Rubber (Hevea) hydrochloride	Hevea-rubber derivative	$\begin{array}{c} \text{CH}_3 \\ \\ -\text{CH}_2-\text{CH}-\text{CCl}-\text{CH}_2- \end{array}$	Pliofilm
Saran†	Vinyl addition	Structure (2-E), Secs. 414ff.	Geon, Velon
Silicones: Resins Rubbers	Condensation	Eqs. (2-1), (5-8)	DC resins Silastic
Silk	Natural polyamide	Table 4-10, structure (5-F)	
Styrene	Vinyl addition	Eq. (1-15), Secs. 414ff.	Lustron Styron
Styrene-isobutylene	Vinyl addition		S-polymer
Styrene rubber (usually applied to copolymers with higher styrene content than ordinary buta S) (see Buta S)			Styraloy
Sulfonamide-formaldehyde resins	Amine-aldehyde condensation	$\begin{array}{c} -\text{N}-\text{CH}_2- \\ \\ \text{SO}_2 \\ \\ \text{C}_6\text{H}_4\text{CH}_3 \end{array}$	Santolite
Tetrafluoroethylene	Vinyl addition	$-\text{CF}_2-$	Teflon
Thioplast	Condensation	Table 1-1, Eq. (1-5a)	Thiokol

Chemical family, common or generic name (none of these is protected by trade-mark)	Chemical nature or polymerization type	Mer	Representative trade names*
Turpentine resins	Vinyl addition		Piccolyte
Urea-formaldehyde	Amine-aldehyde condensation	Sec. 1437	Beetle, Plaskon, Uformite
Vinyl acetate	Vinyl addition	Table 2-11, Secs. 414 <i>f</i> .	Gelva, Elvacet, Vinylite A
Vinyl alcohol	Vinyl derivative	Eq. (10-21)	Elvanol, Resistoflex
Vinyl butyral	Vinyl acetal	Eq. (10-22)	Butacite, Butvar, Saflax, Vinylite X
Vinyl carbazole	Vinyl addition		Polectron
Vinyl chloride	Vinyl addition	Eq. 1-4, Secs. 414 <i>f</i> .	Flamenol, Geon, Koroseal, Tygon, Vinylite Q
Vinyl chloride-acetate	Vinyl addition	Secs. 414 <i>f</i> .	Vinylite V, Vinyon (fiber)
Vinyl chloride-acrylonitrile	Vinyl addition	Secs. 414 <i>f</i> .	Vinyon N (fiber)
Vinyl fluoride	Vinyl addition	Secs. 414 <i>f</i> .	
Vinyl formal	Vinyl acetal	Eq. (10-22)	Formvar
Vinylidene chloride (see Saran)	Vinyl addition	Table 1-1, Secs. 414 <i>f</i> .	
Vulcanized fibre	Zinc-chloride-treated cellulose	Sec. 436	Vulcoid
Wool	Natural polyamide	Table 4-10, structure (4-M)	

* Many companies use a combination of firm name with the common name for the polymer, e.g., Bakelite phenolic, Du Pont polythene, G-E silicone rubber, Hercules ethyl cellulose, and Nixon cellulose nitrate.

† Terms made up to designate particular synthetic polymers and allowed to become generic. Properly written with lower-case initial letter.

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Most synthetic addition polymers are indexed under the monomer, *e.g.*, for polystyrene see Styrene polymers. However, polyethylene is indexed under Polythene, a coined generic name. Condensation polymers are indexed either under the reactants, *e.g.*, Urea-aldehyde resins, or under the polymer linkage, *e.g.*, Polyamides, polyesters.

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